Chemistry of N-Thiosulfinylamines

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CHEMISTRY OF *N*-THIOSULFINYLAMINES

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INTRODUCTION

Compounds containing an *N*-thiosulfinylamino group ($-N=S=S$) fall in the category of S(IV)-thiocumulenes ($X=S=Y$) listed in Table I. Among these thiocumulenes sulfur dioxide, sulfines, and *N*-sulfinylamines ($R-N=S=O$) have been studied extensively, but other members, especially those in which either X or Y is a third-period element, have scarcely been studied, although they are indispensable for a systematic study of various combinations of X and Y.[1] The first successful isolation of stable *N*-thiosulfinyl-amino compounds in 1974,[2] however, has much contributed to the chemistry of S(IV)-thiocumulenes. This article describes the properties of *N*-thiosulfinylamino compounds in relation to the properties of other S(IV)-thiocumulenes, all references to *N*-thiosulfinylamino compounds published before August 1981 being covered.

PREPARATION

The synthesis of compounds containing the *N*-thiosulfinylamino group ($-N=S=S$) was achieved through such simple reactions as those of primary amines ($R-NH_2$) with S_2X_2 or nitroso compounds ($R-N=O$) with thiating reagents like phosphorus penta-
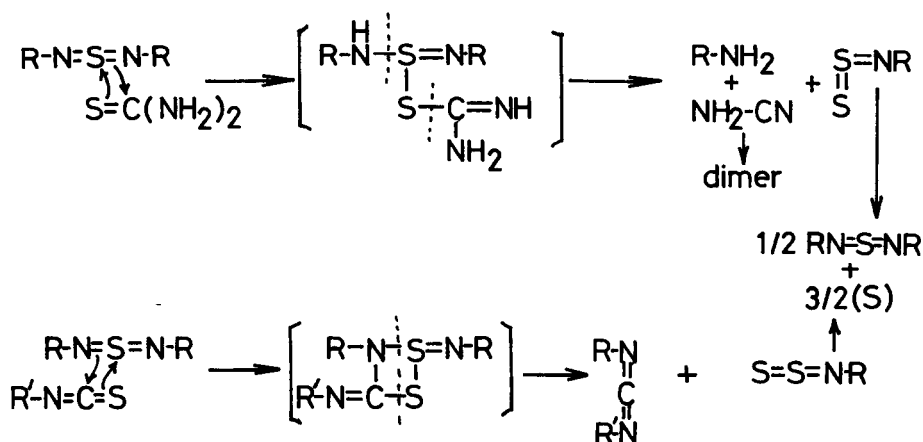
TABLE I

Structure and Nomenclature of S(IV)-Thiocumulenes

X=S=Y	Nomenclature
O=S=O	sulfur dioxide
R—N=S=O	*N*-sulfinylamine
RRC=S=O	sulfine
R—N=S=N—R	sulfur diimide
O=S=S	disulfur monoxide
R—N=S=S	*N*-thiosulfinylamine
RRC=S=NR	thiocarbonyl *S*-imide
RRC=S=CRR	thiocarbonyl ylide
RRC=S=S	thioxothioketone[1a]

sulfide. The structure of the R group, however, affects the stability of the corresponding *N*-thiosulfinylamino compound, therefore only a few examples have been isolated.

N-Thiosulfinylamines were once postulated as unstable intermediates in the reactions of sulfur diimides with thiourea or isothiocyanates,[3] but no direct evidence was obtained.

In 1974, Barton and Robson isolated *p*-(*N,N*-dimethylamino)-*N*-thiosulfinylaniline,[2] the first example of a stable thiosulfinylamino compound: the thiation of *p*-(*N,N*-dimethylamino)-nitrosobenzene or *p*-(*N,N*-dimethylamino)-*N*-sulfinylaniline with phosphorus pentasulfide afforded the corresponding *N*-thiosulfinylaniline as red purple crystals.
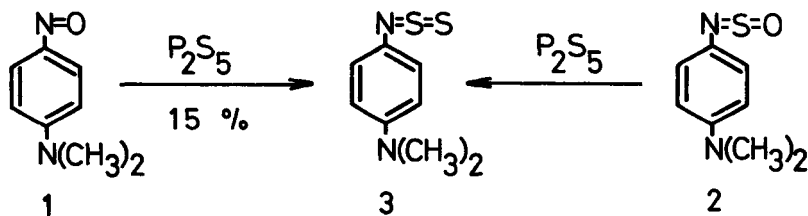
They observed the characteristic UV and visible absorption spectra of this compound when *N,N*-dimethyl-*p*-phenylenediamine was treated with disulfur dichloride or diphthalimido disulfide, but the isolated yields were not given.

Kagami and Motoki obtained *p*-(*N,N*-dimethylamino)-*N*-thiosulfinylaniline by the reaction of diethoxy disulfide with *N,N*-dimethyl-*p*-phenylenediamine in refluxing benzene.[4]
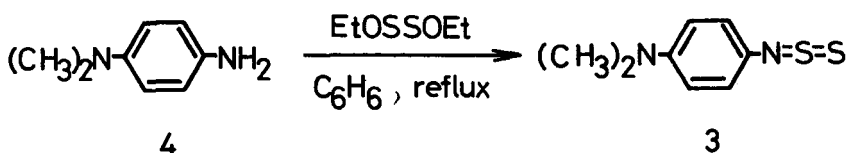
Lawesson's reagent was successfully applied in the thiation of *p*-(*N,N*-dimethylamino)-nitrosobenzene to afford the corresponding *N*-thiosulfinylaniline in a yield as high as 50%.[5]

The present authors obtained 2,4-di-*t*-butyl-6-methyl-*N*-thiosulfinylaniline (**6**) as purple crystals by the reaction of the corresponding aniline with disulfur dichloride.[6] The *N*-thiosulfinylanilines **7** and **8** were prepared in a similar procedure, but they were less stable than **6**.
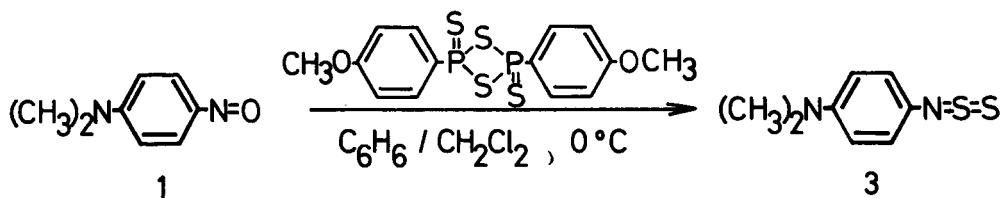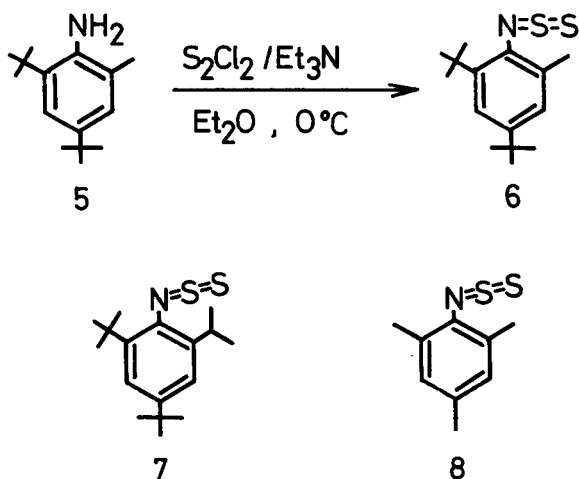
Unlike these anilines, 2,4,6-tri-*t*-butylaniline reacted with disulfur dichloride to give a novel heterocyclic compound, **10a**, which was, however, found to be part of an equilibrium mixture in solution with the *N*-thiosulfinylaniline form (**10b**) being the minor component.[6]
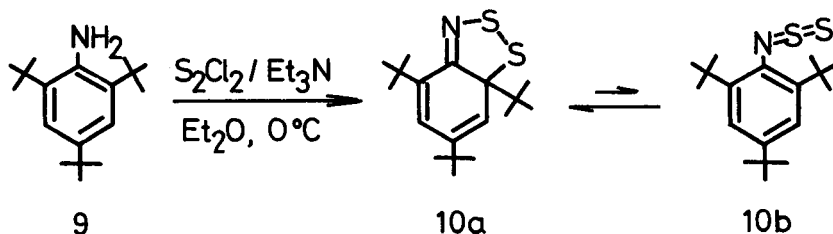
The formation of the *N*-thiosulfinylanilines was discovered during our attempt to prepare stable thionitrosobenzene derivatives. When sterically hindered anilines were treated with sulfur dichloride (SCl$_2$) the corresponding *N*-thiosulfinylanilines were obtained, though in low yields.[6]
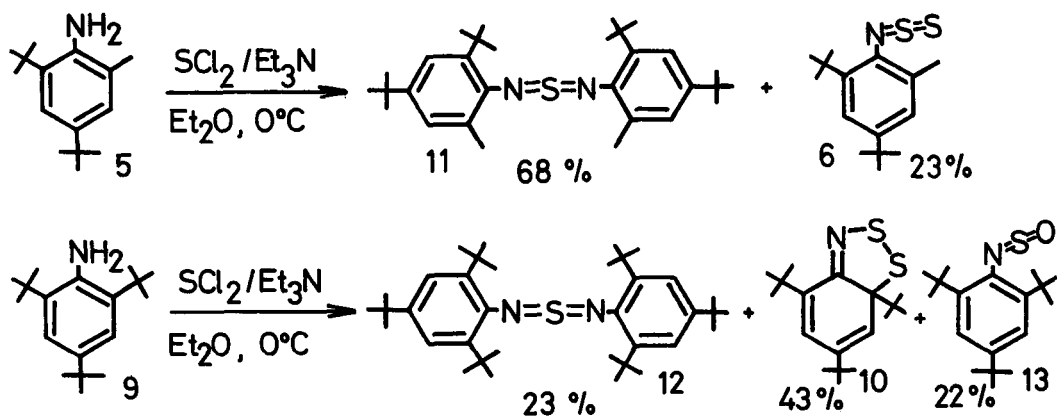
We ascribed the formation of the N-thiosulfinylanilines to the reaction with disulfur dichloride, because sulfur dichloride is known to dissociate partly into disulfur dichloride and chlorine molecule.[7] Use of disulfur dichloride improved the yields of N-thiosulfinylanilines as expected.

Shermolovich *et al.* presented another approach to thiosulfinylamino compounds.[8] Reaction of bis-(trimethylsilyl) sulfide with N-substituted S,S-dichlorosulfur imides afforded the corresponding N-thiosulfinylamines including the first aliphatic examples. These compounds could not be prepared by the reaction of the corresponding amines with disulfur dichloride.[9]

$$R-N=SCl_2 \;+\; S[Si(CH_3)_3]_2 \longrightarrow R-N=S=S$$
$$14 \qquad\qquad\qquad\qquad\qquad\qquad 15$$

$$a: R = t\text{-Bu}; \quad b: R = (CH_3)_2(CN)C; \quad c: 2,4,6\text{-}Br_3C_6H_2$$
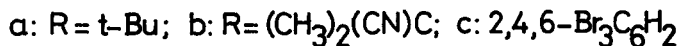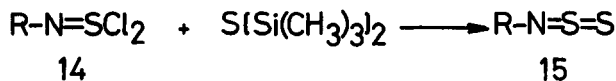
Formation of N-thiosulfinyl-2,4,6-tribromoaniline (**15c**) indicates that the presence of electron-donating groups is not an essential factor for the persistency of the N-thiosulfinylamino group. Attempts to prepare N-thiosulfinylanilines with electron-withdrawing N-substituents, however, resulted in formation of the corresponding sulfur diimides.[8]

$$ArSO_2N=SCl_2 \xrightarrow{\;S[Si(CH_3)_3]_2\;} ArSO_2N=S=NSO_2Ar$$
$$16 \qquad\qquad\qquad\qquad\qquad 17$$

$$Ar= C_6H_5, \quad p\text{-}CH_3C_6H_4, \quad p\text{-}ClC_6H_4, \quad p\text{-}NO_2C_6H_4$$

$$C_6F_5N=SCl_2 \xrightarrow{\;S[Si(CH_3)_3]_2\;} C_6F_5N=S=NC_6F_5$$
$$18 \qquad\qquad\qquad\qquad 19$$
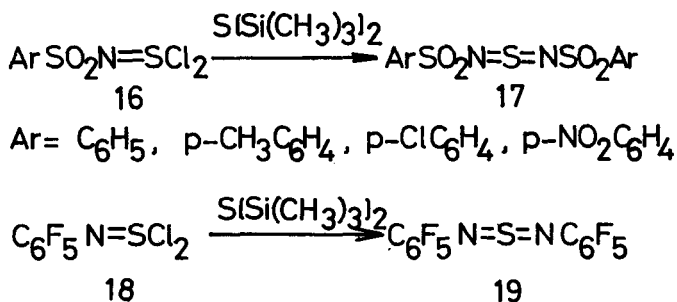
Morimura *et al.* introduced an N-thiosulfinylamino group on a divalent sulfur atom. Treatment of the piperidine derivatives **20a–20e** with disulfur dichloride followed by aqueous ammonia afforded the 1-(thiosulfinylaminothio)-piperidines (**21**) as minor products, the major products being the trisulfides **22**.[10,11]

20

a: X=CH$_2$; b: X= C=O ;

c: X= C$\overset{O}{\underset{O}{<}}$] ; d: X=CHOH;

e: X=PhCOOCH
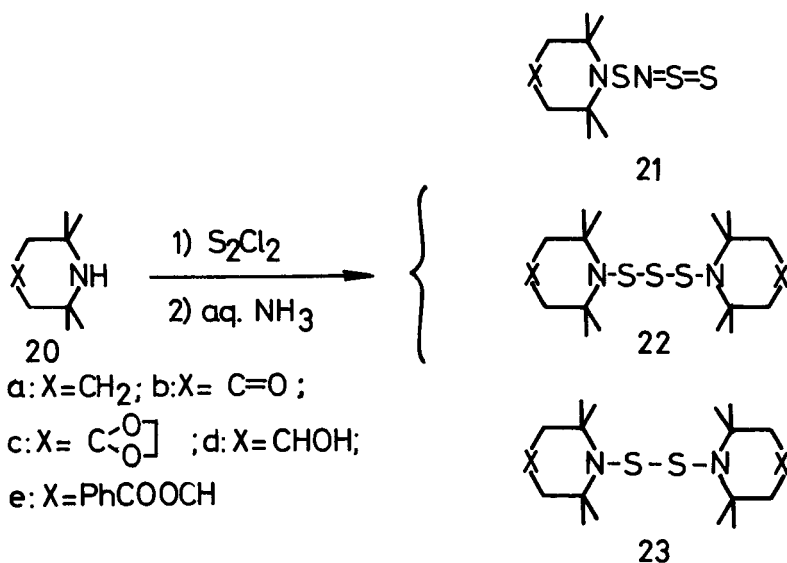
The yield was improved up to 35% by treating the disulfides (**23**) or trisulfides (**22**) with aqueous ammonia in the presence of disulfur dichloride. The sterically unhindered derivatives (**25**) were prepared similarly, though in much lower yield (0.4%).

24 **25**

a: Z = CH$_2$; b: Z= C$\overset{O}{\underset{O}{<}}$]
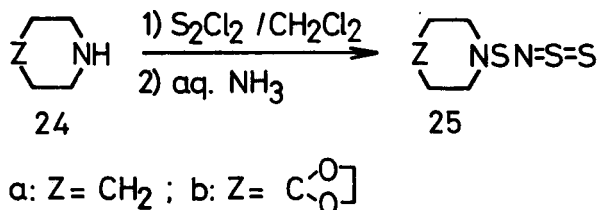
Steric congestion around the N-thiosulfinylamino group in these piperidine derivatives is not an essential factor for the persistency of this functional group, since no detectable change in visible absorption was observed when both the sterically hindered compounds (**21a–21e**), and the unhindered one (**25a**) were refluxed in chloroform for 3 hours.

Chivers and Oakley found another type of —S—N=S=S compound during a study on the thermal degradation of sulfur-nitrogen compounds.[12] Heating of the cyclotrithiazene (**26**) in refluxing acetonitrile gave N-(thiosulfinylaminothio)-iminotriphenylphosphorane (**27**).

26 **27**
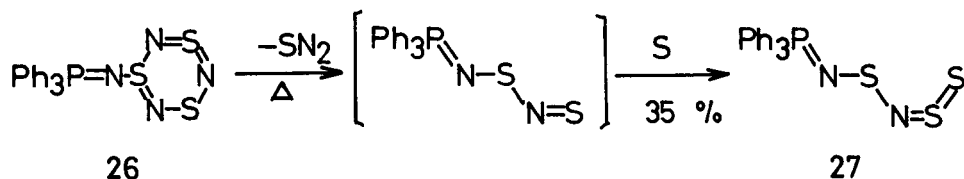
There have been reported some reactions which probably proceed via intermediate N-thiosulfinylamines.

The reaction of N,N-bis-(trimethylsilyl)-amines with S$_2$Cl$_2$ is reported to give sulfur diimides, probably via an N-thiosulfinylamine intermediate.[13]

$$R\text{-}N(SiMe_3)_2 \; + \; S_2Cl_2 \longrightarrow [R\text{-}N{=}S{=}S] \longrightarrow R\text{-}N{=}S{=}N\text{-}R$$
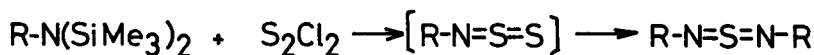
$$(R = \; aryl, \; alkyl)$$

The reaction of primary aralkylamines[4] or arylhydrazines[14] with diethoxy disulfide proceeds as illustrated below. The presence of an α-hydrogen atom apparently diminishes the stability of the N-thiosulfinylamine structure.

$$ArCH_2NH_2 \xrightarrow{\text{EtOSSOEt}} [ArCH_2N{=}S{=}S] \longrightarrow [ArCH{=}NSSH]$$

Ar: phenyl,
     furyl

$$\xrightarrow{\text{EtOSSOEt}} [ArCH{=}N\text{-}S_6N{=}CHAr]$$

$$\longrightarrow ArCH{=}N\text{-}S_4N{=}CHAr$$

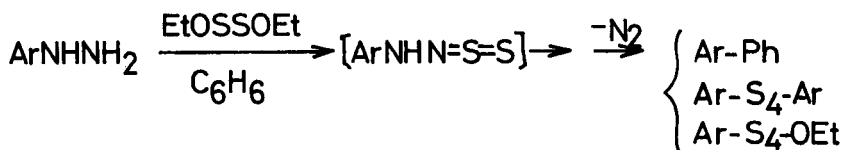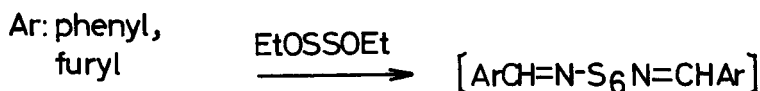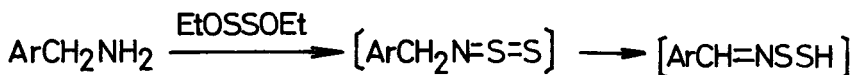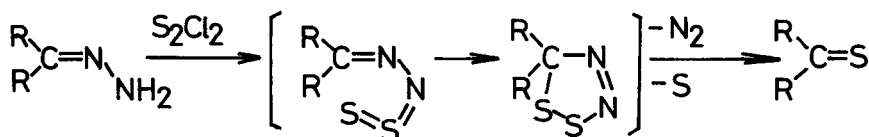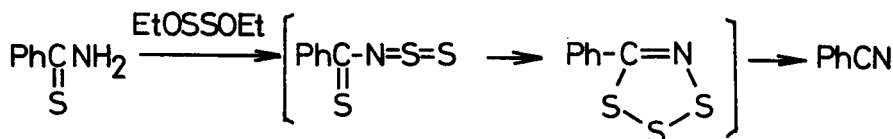$$ArNHNH_2 \xrightarrow[C_6H_6]{\text{EtOSSOEt}} [ArNHN{=}S{=}S] \xrightarrow{-N_2} \begin{cases} Ar\text{-}Ph \\ Ar\text{-}S_4\text{-}Ar \\ Ar\text{-}S_4\text{-}OEt \end{cases}$$

Reactive multiple bonds adjacent to the N-thiosulfinylamino group may be a destabilizing factor. Diethoxy disulfide reacts with thiobenzamide, but, interestingly, not with benzamide, to give benzonitrile,[4] and reactions of hydrazones with disulfur dichloride proceed likewise to provide a new method for thioketone preparation.[15,16]

$$\underset{S}{\overset{PhC}{\|}}NH_2 \xrightarrow{\text{EtOSSOEt}} \left[\underset{S}{\overset{PhC\text{-}N{=}S{=}S}{\|}} \longrightarrow \underset{S\diagdown S \diagup S}{Ph\text{-}C{=}N} \right] \longrightarrow PhCN$$

$$\underset{R}{\overset{R}{}}C{=}N{\diagdown}NH_2 \xrightarrow{S_2Cl_2} \left[\underset{R}{\overset{R}{}}C{=}N{\diagdown}\underset{S{=}S}{N} \longrightarrow \underset{R}{\overset{R}{}}C{\diagup}\overset{N}{\underset{S\text{-}S}{}}N \right] \xrightarrow[-S]{-N_2} \underset{R}{\overset{R}{}}C{=}S$$

The reaction of β-ketoenamines (28) with disulfur dichloride also proceeds similarly.[17] In this case, however, the intramolecularly cyclized species are isolable providing a general method for the synthesis of 5H-1,2,3-dithiazoles (29). This heterocycle does not appear to dissociate into the open-chain N-thiosulfinylamine form. When β-ketoenamines bearing β-hydrogen (30) were employed, the corresponding 5H-1,2,3-dithiazoles were not obtained. The reaction in the presence of methanol, however, resulted in the formation of methoxy substituted 5H-1,2,3-dithiazoles (31), which suggests the involvement of dithiazolium ions (32).[17]
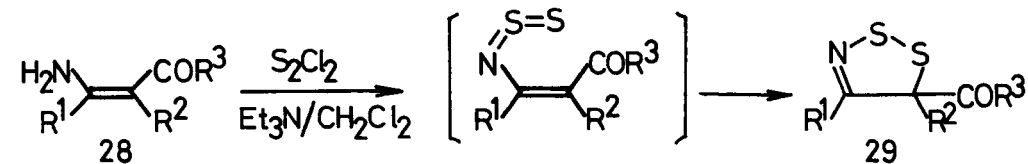
a: $R^1 = R^2 = R^3 = CH_3$

b: $R^1R^2 = (CH_2)_4$, $R^3 = OC_2H_5$

c: $R^1 = C_6H_5$, $R^2 = R^3 = CH_3$

$\dfrac{S_2Cl_2/Et_3N}{CH_3OH/CH_2Cl_2}$

a: $R^3 = CH_3$

b: $R^3 = OC_2H_5$

$-HCl$

$-2S$
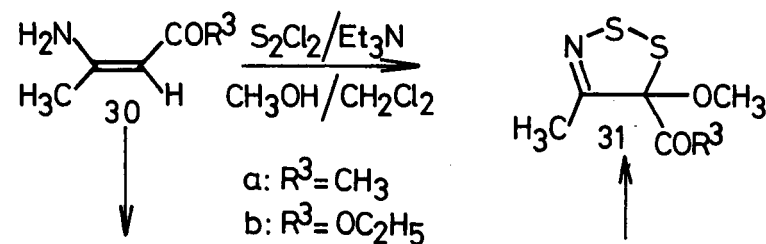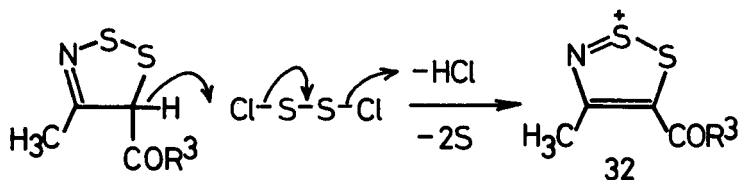
In view of the above findings as well as of the equilibrium between **10a** and **10b** the mechanism of the Herz reaction[18,19] can be accounted for as follows. Chlorination of the benzene ring of the dithiazolium ion with disulfur dichloride was proposed by Mayer *et al.*[19,20]

$-S_2$

$-RCl$
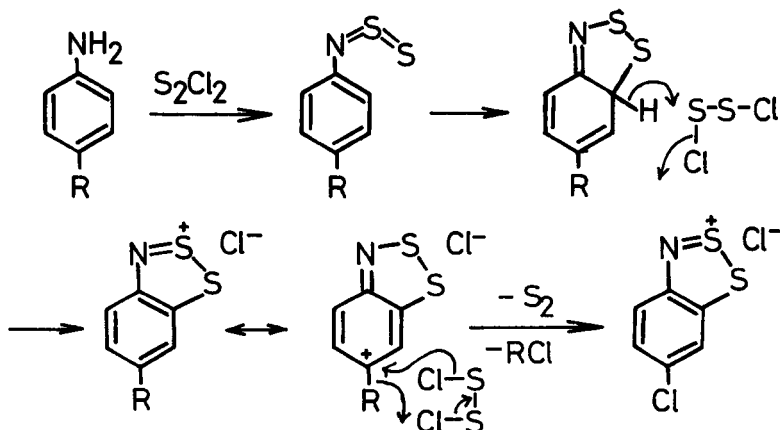
Introduction of two *ortho*-substituents or strongly electron-donating substituents on the starting aniline prevents the Herz reaction, thus resulting in formation of *N*-thiosulfinylanilines as described previously.

STRUCTURE AND BONDING

(1) Geometry The geometrical features of the *N*-thiosulfinylamino group are summarized in Table II. The bent structure ($\angle$NSS $\sim$ 120°), a common characteristic of

TABLE II

The Geometry of the —N=S=S Group as Determined by X-Ray Crystallographic Analysis

Compounds	Bond lengths (Å)		Angles (degree)		Reference
X—N=S=S	N=S(IV)	S(IV)=S(II)	∠XNS	∠NSS	
6	1.548	1.898	126.4	119.7	21
21c	1.569	1.912	119.2	114.9	11
27	1.592	1.908	120.9	111.4	12

S(IV)-cumulenes of the type X=S=Y, suggests 3-center-4-electron π-bonding with an sp^2-hybridized sulfur atom as the central atom. The S=S bonds are longer than those in S=S (1.892 Å),[22] S=S=O (1.882 Å),[23] and S=SF$_2$ (1.868 Å),[24] but shorter than those in ClS—SCl (1.931 Å)[25] and CH$_3$S—SCH$_3$ (2.03 Å),[26] confirming that the S=S bond of the —N=S=S group has a weak double-bond nature.

Compared with the C—N=S=S group in the N-thiosulfinylaniline (6), the S—N=S=S groups in compounds 21c and 27 have longer S=S and N=S bond lengths and smaller ∠NSS angles. These deviations suggest that the S(II) atom attached to the nitrogen atom of the S—N=S=S group enhances the contribution of the following polarized structures:

$$—S—N=S=S \leftrightarrow —\overset{+}{S}=N—\overset{-}{S}=S \leftrightarrow —\overset{+}{S}=N—S—\overset{-}{S}$$

A similar polarization effect may be expected for p-(N,N-dimethylamino)-N-thiosulfinyl-aniline (3), but the geometry of this compound unfortunately remains undetermined.

In each of the compounds listed in Table II, the X—N bond and the S=S bond are in the Z-configuration with respect to the N=S bond. Interestingly, the N-sulfinylamines 13[27] and 33[28] were also found to have Z-configuration. The cause for this preference of the Z-configuration, a common characteristic of thiocumulenes X=S=N—, is unclear, but a repulsive interaction between the X atom and the lone pair electrons of the N atom seems to be important.
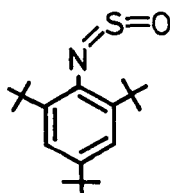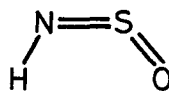
13   33

The NMR spectrum of 6 in CD$_2$Cl$_2$ solution showed the presence of two t-butyl groups, one methyl group, and two aromatic protons, and the number of the signal peaks was unchanged over a temperature range of −102 ∼ +70°C,[29] suggesting the existence of only one form, probably with Z-configuration, also in solution. Although in solution 10b exists in an equilibrium mixture with the cyclized form 10a the structure in the crys-
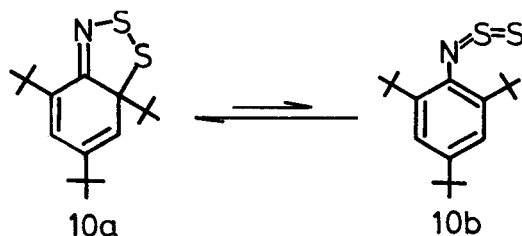
10a   **10b**

alline state was confirmed by X-ray analysis to be the cyclized form.[30] As interconversion between **10a** and **10b** was slow enough to give rise to two sets of NMR signals due to the two tautomers the equilibrium constants, K = [**10a**]/[**10b**], were measured over a temperature range of 11°C (K = 19.5) ~ 63°C (K = 5.1) in carbon tetrachloride solution. Over the temperature range studied the major component was **10a**, but the relative amount of **10b** increased with increasing temperature. The enthalpy (ΔH) and the entropy of isomerization (ΔS) were estimated to be −4.9 kcal mol^{-1} and −11.3 cal mol^{-1} deg^{-1}, respectively. These thermodynamic quantities bear a striking resemblance to those reported for the azidoimidine-tetrazole equilibrium;[31] for instance, ΔH and ΔS of the equilibrium between 2-azidopyrimidine and tetrazole[1,5-a]pyrimidine (**34**) were reported to be −5.1 kcal mol^{-1} and −11.1 cal mol^{-1} deg^{-1}, respectively, in dimethyl sulfoxide-d_6.[32]

34a   **34b**
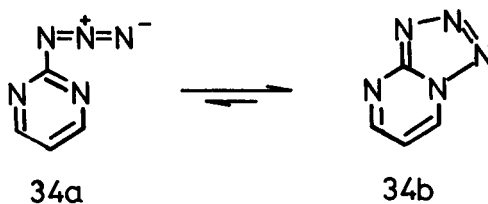
The similarity of these thermodynamic quantities, however, is somewhat surprising considering that the azidoimine-tetrazole reaction is a 6π-to-10π conversion without loss of aromaticity, at least in a formal sense, while the *N*-thiosulfinylamine-dithiazole reaction is accompanied by complete loss of aromaticity.

The exothermicity of this unusual ring formation of **10b** into **10a** may be attributable to both decreased aromaticity due to steric congestion by three adjacent bulky groups and the high reactivity of the *N*-thiosulfinylamino group towards double bonds as demonstrated by the 1,3-dipolar addition of *p*-(*N,N*-dimethylamino)-*N*-thiosulfinylaniline (**3**) to olefins.[2]

Equilibrium constants at 43°C in various solvents[29] are shown in Table III, where it is demonstrated that polar solvents greatly enhance the preference for the cyclic isomer **10a**, suggesting that the dipole moment of **10a** is larger than that of the *N*-thiosulfinylaniline **10b**. Actually, the dipole moment of **10a** (ca. 2.9 D)[33] is larger than that of **10b** which, in a reasonable estimate, was assumed to be nearly equal to the dipole moment of **6** (1.51 D).[34] Interestingly, quite a similar solvent effect has been reported for azidotetrazole equilibria.[35] Thus, in less polar solvents, the equilibrium is shifted towards the side of the azido form suggesting that the dipole moment of the azide form is smaller than that of the tetrazole form. This situation is in accordance with the fact that the dipole moment of phenyl azide (1.56 D)[36] is smaller than that of 1,2,3-benzotriazole (4.10 D).[36]

TABLE III

Solvent Effect on K at 43°C

Solvent	Dielectric const.	K = [10a]/[10b]
Hexane	1.89	6.3
Cyclohexane	2.02	8.6
Carbon tetrachloride	2.23	9.2
Ethyl acetate	6.02	14.5
Dichloromethane-d_2	9.08	12.2
Acetone-d_6	20.7	17.7
Acetonitrile	37.5	25

The structural differences among the thiocumulenes X=S=Y including —N=S=S can be related to the electronegativities of X and Y.[1] The bond lengths of the S=O bonds in X=S=O and those of the S=N bonds in Y=S=N— are plotted linearly against the electronegativities of X and Y, respectively (Figure 1). The bond lengths employed in Figure 1 are listed in Table IV. In the case of the sulfur diimide, the bond length of the N=S bond with Z-configuration of N,N'-bis-(4-methylphenyl)-sulfur diimide was used. The S=O bond of X=S=O and the S=N bond of Y=S=N are shortened and thus strengthened, as the electronegativity of X or Y increases. This correlation may be interpreted in terms of molecular orbital considerations. The Hückel
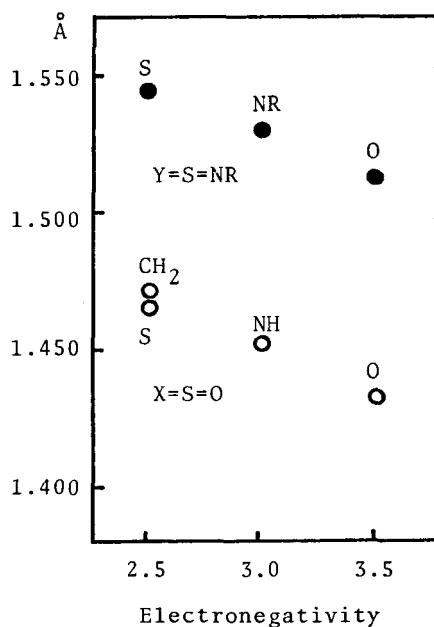

FIGURE 1.   The relationship between the S=O bond length of X=S=O and the electronegativity of X (○), and between the S=N bond length of Y=S=NR and the electronegativity of Y (●).

TABLE IV

Bond Lengths of Thiocumulenes X=S=Y

X=S=Y	N=S (Å)	S=O (Å)	Reference
SO$_2$	—	1.431	37a
HNSO	1.512	1.451	28
H$_2$CSO	—	1.469	37b
p-Tol-NSN-p-Tol	1.53	—	37c
Ar-NSS	1.548	—	21

p-Tol: p-Methylphenyl

Ar: 2,4-Di-t-butyl-6-methylphenyl

molecular orbitals (HMO) of the allyl anion type are illustrated in Figure 2,[57] where substitution of the terminal carbon atoms by an electronegative atom X (Coulomb integral = $\alpha + \beta$; exchange integrals with respect to adjacent atoms = β; and exchange integrals with respect to nonadjacent atoms = 0) depresses the energies of the occupied orbitals. Therefore, the 3-center-4-electron π bond of X=S=Y, which is isoelectronic with the allyl anion, is strengthened by increasing electronegativity of X and Y.

(2) The charge distribution in the N-thiosulfinylamino group   ESCA spectra are very useful in the elucidation of the electronic structures of S(IV)-cumulenes such as —N=S=O, —N=S=N—, and —N=S=S.

   Figure 3 shows the N1s and S2p binding energies of thiocumulenes (X=S=N—) as determined by ESCA.[38] The N-thiosulfinylaniline **6** showed two peaks in the S2p spectrum, *i.e.* at 165.5 and 163.4 eV. Since the lower value, 163.4 eV, is similar to the binding energy of carbon disulfide (163.9 eV)[39] or that of 1,3-dithiolane-2-thione (163.4 eV),[39] it can be assigned to the terminal sulfur atom of the N-thiosulfinylamino group. The

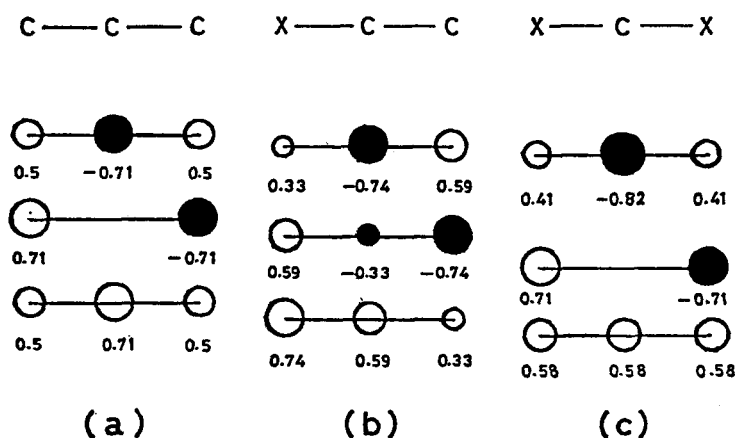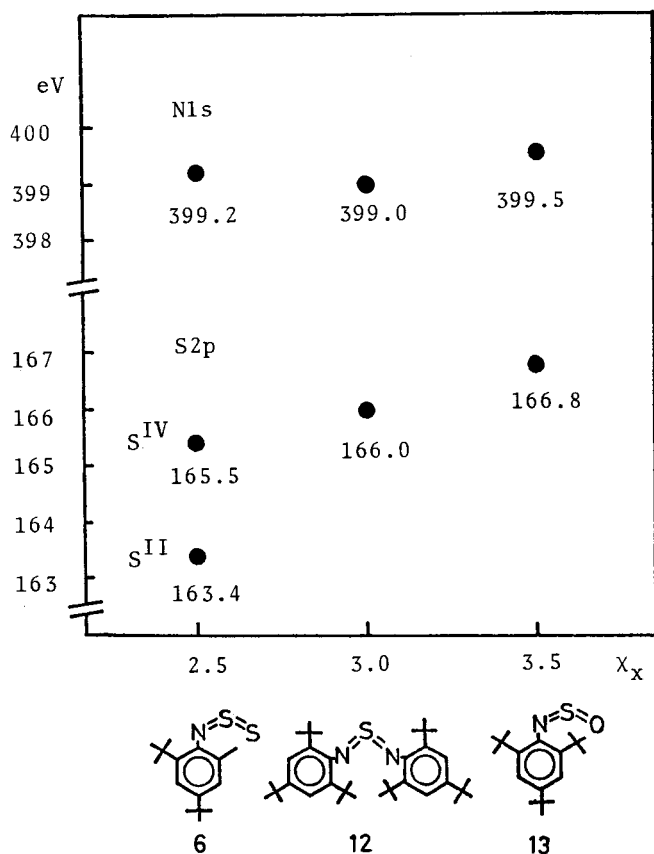FIGURE 2.   Changes in the allyl-type HMOs caused by the introduction of electronegative atoms X.

FIGURE 3.   N1s and S2p binding energy of N=S=X.

higher value, 165.5 eV, can be attributed to the central sulfur atom of the N-thiosulfinyl-amino group, but is slightly lower than those of sulfoxides and other compounds containing tricoordinated sulfur atoms (about 166 eV),[39] suggesting less positive charge on the sulfur atom.

As shown in Figure 3, a linear correlation exists between the S2p binding energies of —N=S=X (X = N, O, S) and the electronegativity of X (Pauling's scale). The larger the electronegativity of X, the more positive in charge is the central sulfur atom, thus enhancing its binding energy. However, the N1s binding energy of the thiosulfinylamino group showed an intermediate value between those of the sulfur diimide 12 and the N-sulfinylamine 13. This situation may be interpreted in terms of differences in the bonding nature of X=S=N—. Negative charge in the N-sulfinylamino group may be highly localized on the oxygen atom because of the large electronegativity of oxygen and therefore the negative charge on the sulfur atom or the nitrogen atom is small to show a high binding energy in the ESCA spectra. Negative charge in the sulfur diimide may be localized equally on the two nitrogen atoms to show low binding energy of the N1s electrons. As the sum of the electronegativities of the two ligand atoms (two nitrogen atoms, 6.0) of a sulfur diimide is smaller than that in the N-sulfinylamino group (6.5), the S2p binding energy of a sulfur diimide is smaller than that of an N-sulfinylamino group. In the case of the N-thiosulfinylamino group, the delocalization of the four π-electrons over

the three atoms may be enhanced to make the charge separation smaller because the sum of the electronegativities of the two ligand atoms, N and S, of the *N*-thiosulfinyla-mino group is smaller than those of *N*-sulfinylamines or sulfur diimides. Therefore, the S2p binding energy of the *N*-thiosulfinylamino group is smaller than those of the *N*-sul-finylamino group and sulfur diimides, but the N1s binding energy is larger than that of sulfur diimides.

The dipole moment of 2,4-di-*t*-butyl-6-methyl-*N*-thiosulfinylaniline (**6**) is 1.51 D (in benzene at 25°C),[34] and the bond moments have been estimated to be 2.60 D for the S(IV)=S(II) ($\rightarrow$) bond and 0.55 D for the N=S(IV) ($\leftarrow$) bond. Therefore, the negative charge on the terminal sulfur atom and that on the nitrogen atom of the *N*-thiosulfinyl-amino group are estimated to be 1.37×10^{-10} and 3.56×10^{-11} e.s.u. using the S=S and S=N bond lengths determined for **6** (1.898 and 1.548 Å, respectively) (Figure 4). Sim-ilarly, the negative charges on the N and O atoms of the *N*-sulfinylamino group in Ph—N=S=O have been estimated to be 2.7×10^{-11} and 2.46×10^{-10} e.s.u., using van Woerden's values ($\mu_{S-O} = 3.4$ D, $\mu_{S-N} = 0.4$ D)[40] and the S=O and S=N bond lengths determined for *N*-sulfinyl-2,4,6-tri-*t*-butylaniline (1.441 and 1.479 Å, respectively). Therefore the negative charge on the nitrogen atom of the *N*-thiosulfinylamino group is 1.32 times that of the *N*-sulfinylamino group, and the negative charge on the divalent sulfur atom of the *N*-thiosulfinylamino group is 0.58 times the charge on the oxygen atom of an *N*-sulfinylamine. Thus, the charge separation in the *N*-thiosulfinylamino group is much smaller than that of the *N*-sulfinylamino group. This conclusion is in good agreement with the ESCA data presented above.

It is worth noting that the terminal sulfur atom of the *N*-thiosulfinylamino group bears more negative charge than the nitrogen atom although the electronegativity of sulfur is smaller than that of nitrogen because it implies that the S=S bond is a coordi-nation bond.
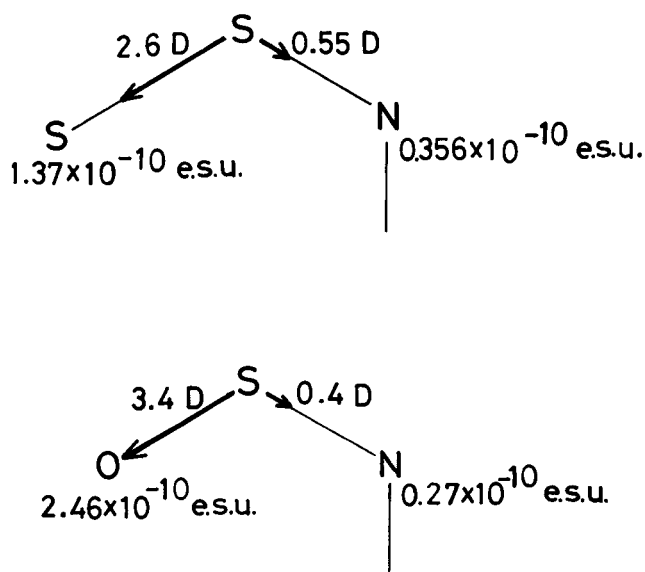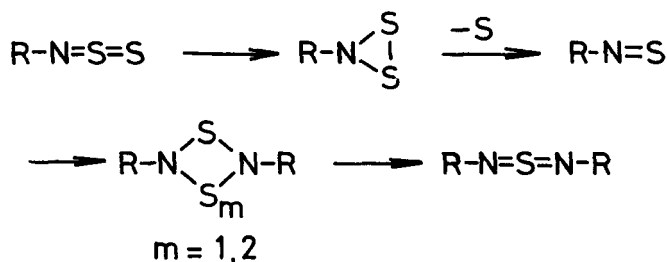

FIGURE 4. Bond Moments and Charge Distribution in the *N*-Thiosulfinylamino and the *N*-Sulfinyl-amino Group.
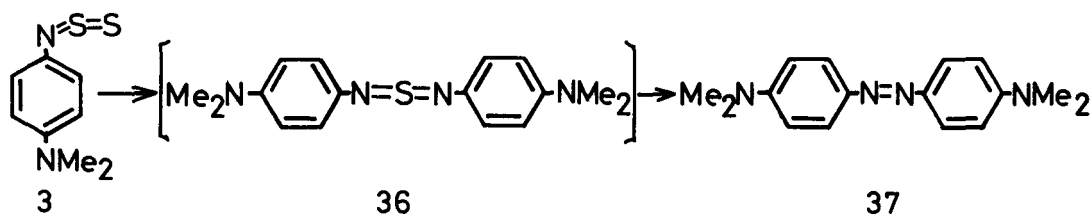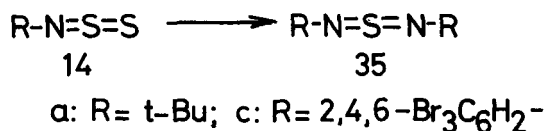
REACTIONS

(*1*) *Thermolysis*   Since the thiocumulenes, X=S=Y, have a 4π-electron system like that of the allyl anion they have the common characteristic property of undergoing conrotatory thermal cyclizations into 3-membered rings which is often followed by extrusion of a sulfur atom: thiocarbonyl *S*-imides give imines and thiones,[41] a sulfine gives a ketone,[42] and *N,N'*-diarylsulfur diimides give azoarenes.[43]

By analogy with these thiocumulenes it is to be expected that the thermal degradation of *N*-thiosulfinylamino compounds probably proceeds through a similar pathway to give unstable thionitroso compounds.

$$ R-N=S=S \longrightarrow R-N\begin{smallmatrix}S\\|\\S\end{smallmatrix} \xrightarrow{-S} R-N=S $$

$$ \longrightarrow R-N\begin{smallmatrix}S\\\\S_m\end{smallmatrix}N-R \longrightarrow R-N=S=N-R $$
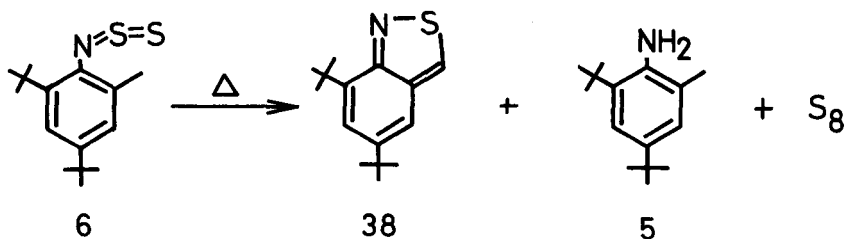
$$ m = 1,2 $$

Scheme 1

If we assume that generation of thionitroso intermediates results in formation of sulfur diimides as described in the above scheme, most of the following pyrolytic behavior of *N*-thiosulfinylamino compounds can be explained. The compounds **14a** and **14c** on heating at 100°C give the corresponding sulfur diimides,[8] and the compound **3**, gave the corresponding azoarene at 200°C.[2]

$$ R-N=S=S \longrightarrow R-N=S=N-R $$
$$ \quad\;\; 14 \qquad\qquad\qquad 35 $$

a: R = t-Bu;   c: R = 2,4,6-Br$_3$C$_6$H$_2$-

In the latter case, the sulfur diimide **36** is considered to decompose into the azoarene under the reaction conditions.

When an *N*-thiosulfinylaniline has *ortho*-benzylic hydrogen(s), it exhibits a unique thermal behavior. Heating the *N*-thiosulfinylaniline **6** in refluxing benzene afforded a 2,1-benzisothiazole derivative, **38** (32%), the corresponding aniline, **5** (26%), and sulfur.[44] During the reaction a trace of hydrogen sulfide was detected. This reaction is rem-

iniscent of the thermolysis of 2,4-di-*t*-butyl-6-methylnitrosobenzene (**39**) leading to **41** and **5**,[45] which was found by the authors to proceed as illustrated in the following scheme.[46]
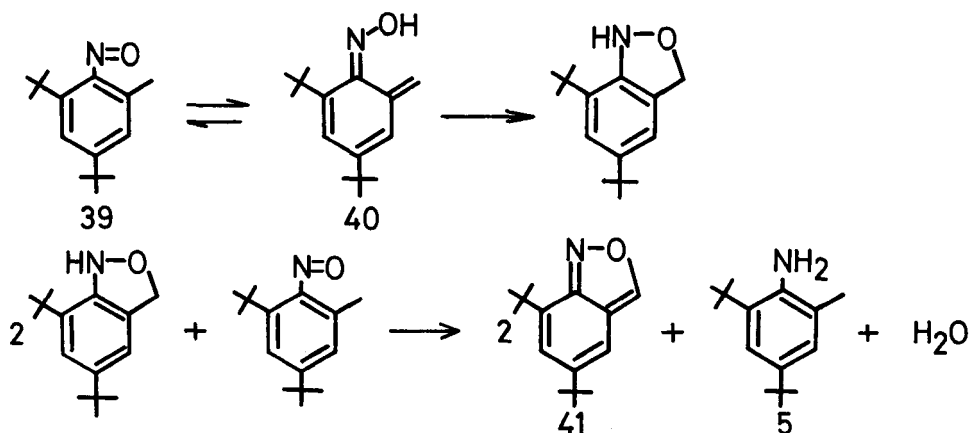
Furthermore, 2,4-di-*t*-butyl-6-ethyl- (**42**) and 2,4-di-*t*-butyl-6-isopropylnitrosobenzene (**43**) have been found to be less stable than **39** and to decompose already at 0–5°C;[46] this order of stability is consistent with the above reaction scheme in which the decomposition starts with a 1,5-hydrogen shift, for the initially formed *o*-quinone imine, **40**, is thought to be more stable starting from **42** or **43** than from **39**.

Considering the similar order of stability observed in the case of *N*-thiosulfinylanilines, *i.e.*, **7** is less stable than **6**, also here the following mechanism starting with a 1,5-hydrogen shift seems to be the most probable pathway.
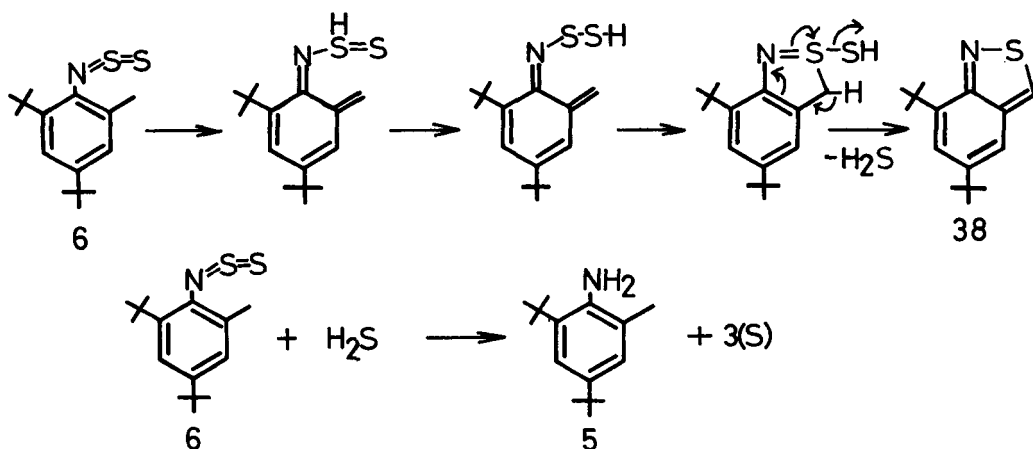
The last step, reduction of **6** with hydrogen sulfide, was confirmed by a separate experiment.

The following alternative pathway involving the thiooxime is also possible; extrusion of sulfur atom from such types of compounds as **44** and **46** are known.[47]
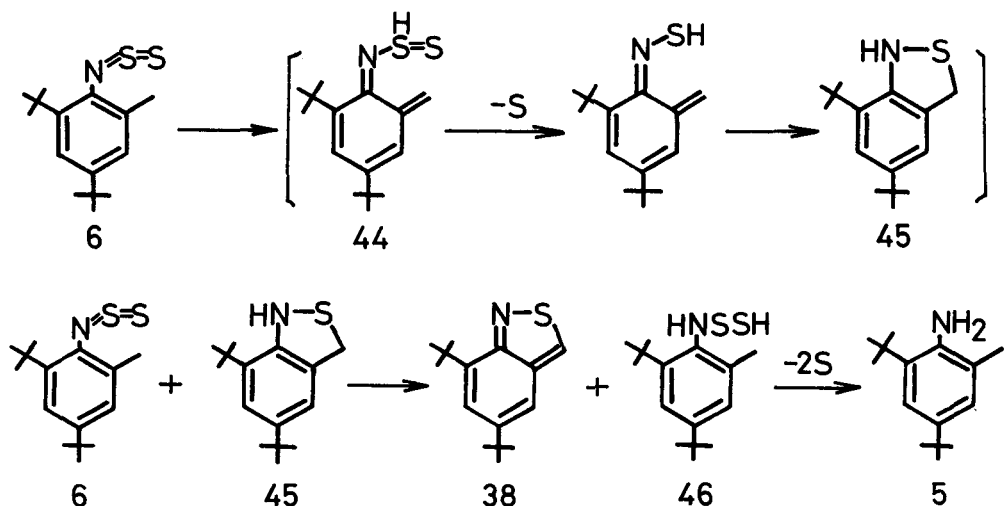
Whichever mechanism is operative these pathways starting with a 1,5-hydrogen shift explain the instability of *N*-thiosulfinylanilines with *ortho*-benzylic hydrogens. Such a 1,5-hydrogen shift involving *ortho*-benzylic hydrogens seems to be a general type of reaction; the sulfur diimide **11** undergoes clean disproportionation into **38** (94%) and **5** (91%) much faster than the thermal degradation of **6**.[44]
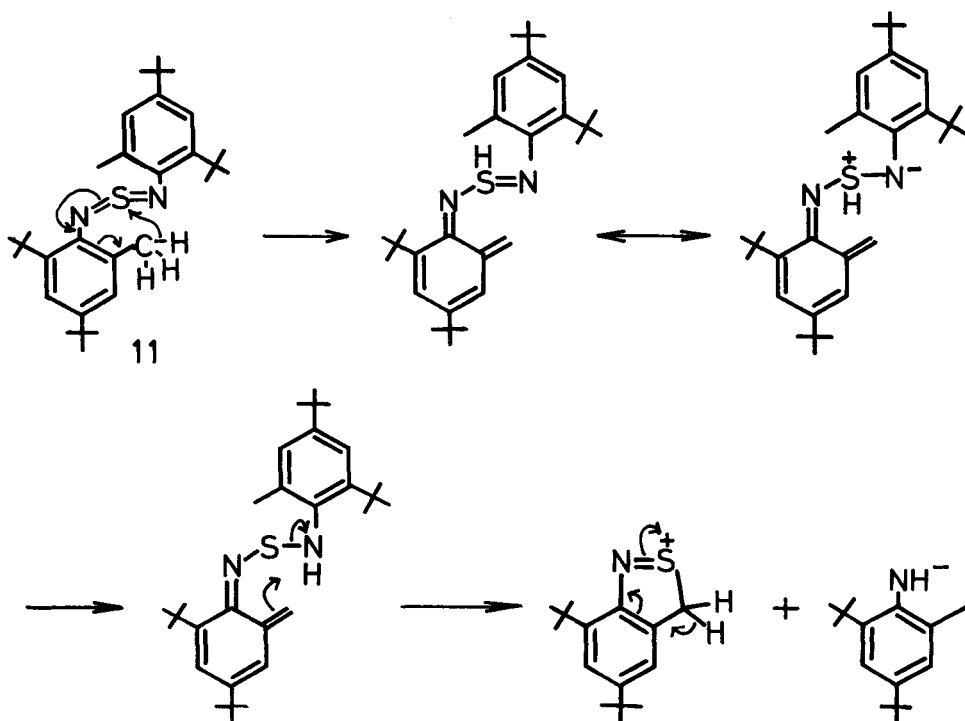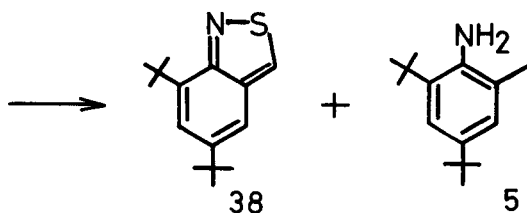
Interestingly, the reaction of 2,5-di-*t*-butylaniline with disulfur dichloride gave the corresponding sulfur diimide **48** instead of the *N*-thiosulfinylaniline **47** which would be no doubt the initial product.[44] The higher stability of **6** compared to **47** may be due to bulky substituents around the *N*-thiosulfinylamino group which hinder the isomerization to a three-membered ring as well as dimerization leading to formation of the sulfur diimide.
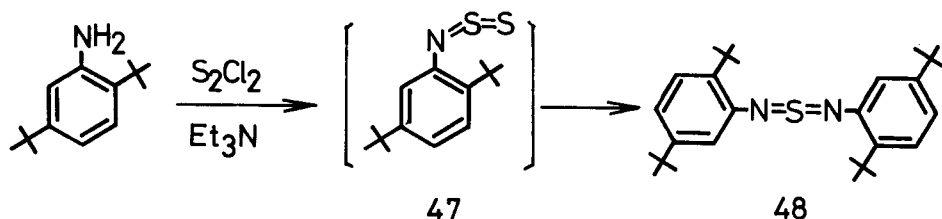

The thermolysis of **6** into **38** and **5** may be rationalized also in terms of an intermediacy of the thionitrosobenzene derivative **49**, which would give **38** and **5** quite similarly to the case of the nitroso derivative. Alternatively, formation of the sulfur diimide **11** followed by its disproportionation is also a possible route giving **38** and **5**. These two pathways involving the formation of the thionitrosobenzene derivative, however, cannot explain the fact that the 6-isopropyl derivative **7** is less stable than the 6-methyl derivative **6**.
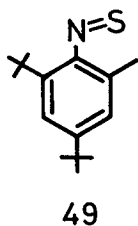

Everything considered we assume that *N*-thiosulfinylanilines decompose via pathways starting with a 1,5-hydrogen shift if the steric protection of the *N*-thiosulfinylamino group is sufficient and benzylic hydrogens are present in the ortho substituent. In the case where the steric protection is insufficient the *N*-thiosulfinylanilines undergo decomposition into the thionitroso intermediate via the corresponding dithiaziridine and subsequent conversion to the sulfur diimide as the final product (see Scheme 1).

Thermolysis of **10** in refluxing benzen gave **50** (21%), **9** (34%), and sulfur (27%).[44] Although the mechanism of formation of **50** is not clear, the oxygen in **50** probably comes from adventitious water.[44] During the reaction a persistent ESR signal ($a_N = 8.2$ G, $g = 2.008$) was observed. This signal was considered to be due to the nitrogen-centered radical **51**, though the alternative structure **52** cannot rigorously be excluded.[44]
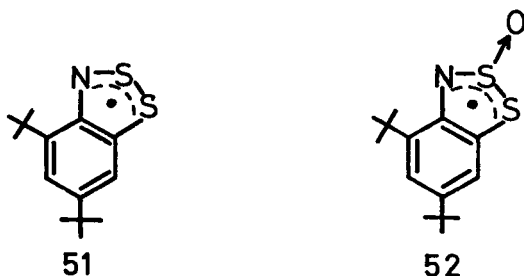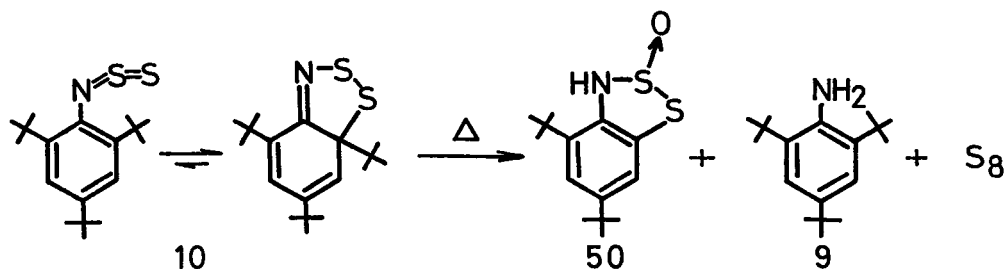
The presence of two sulfur atoms in this radical, however, was confirmed using ESR spectroscopy by Mayer *et al.*[48] They developed a facile microsynthetic approach to benzo-1,2,3-di-thiazolyl radicals.
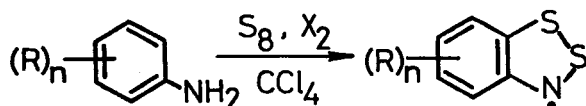
Employment of ^{33}S-enriched (92.25%) sulfur afforded ^{33}S-enriched benzo-1,2,3-dithiazolyl radicals, the ESR spectra of which demonstrated the presence of two ^{33}S atoms in this radical. A series of benzo-1,2,3-dithiazolyl radicals has been prepared and studied by ESR spectroscopy.[48,49,50] They possess characteristically large g-values (ca. 2.008).

(2) *Photolysis*   The photochemical behavior of organic S(IV)-thiocumulenes, X=S=Y, has not been investigated except for that of thiobenzophenone S-oxide where the products are benzophenone and sulfur.[51,52,52a]
Irradiation of **6** affords the sulfur diimide **11**, the aniline **5**, and sulfur.[44]
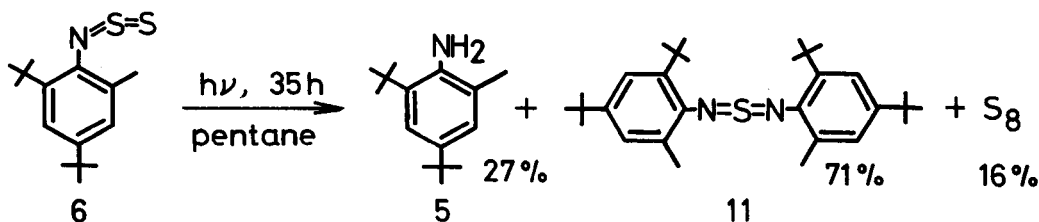
During irradiation of **6** in an EPA matrix, the intensity of the absorption at 340 nm decreased, while a very intense band appeared at 473 nm. The molar extinction coefficient of this species was estimated to be about 1.5×10^4 or more. Since this absorption is different from that of phenyl nitrene[53] and atomic sulfur (or its oligomers)[54] it may be due to either **53** or **54**.

The formation of the aniline **5** is probably due to photodecomposition of the sulfur diimide **11**, since upon irradiation in pentane **11** gave 18% of the aniline **5** with 68% recovery of **11**.
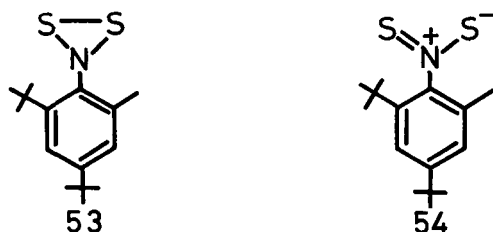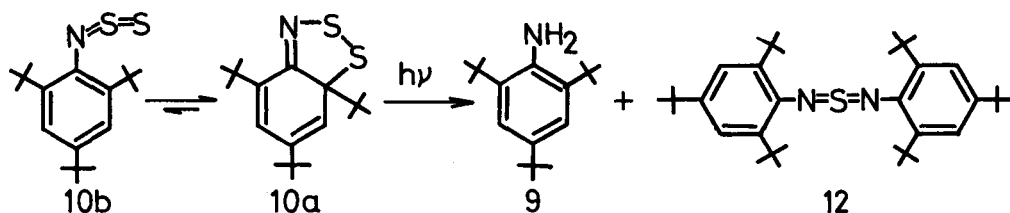

Irradiation of **10** in pentane afforded the sulfur diimide **12** (8%) and the aniline **9** (11%).[44] Since these products are very similar to those of the photoreaction of the *N*-thiosulfinylaniline **6**, the precursor of these products is considered to be the *N*-thiosulfinylaniline **10b**.

(3) The mechanism of the sulfur diimide formation We presented above a reasonable reaction pathway to sulfur diimide from *N*-thiosulfinylaniline via a thionitroso compound. Desulfurization of *N*-thiosulfinylanilines with triphenylphosphine seems to be another pathway to sulfur diimides via thionitrosoarenes.

The reaction of **6** or **10** with an equimolar amount of triphenylphosphine proceeded even at −78°C to give the products shown below.[55]
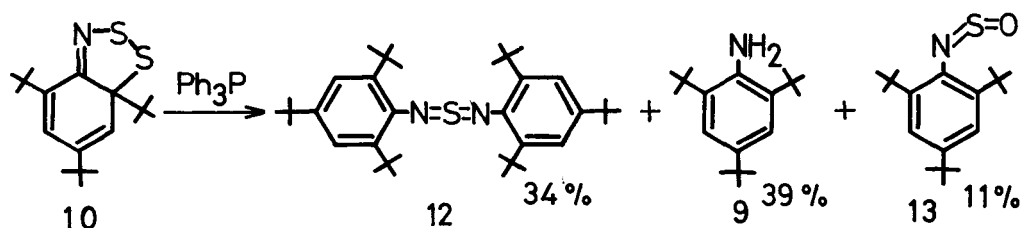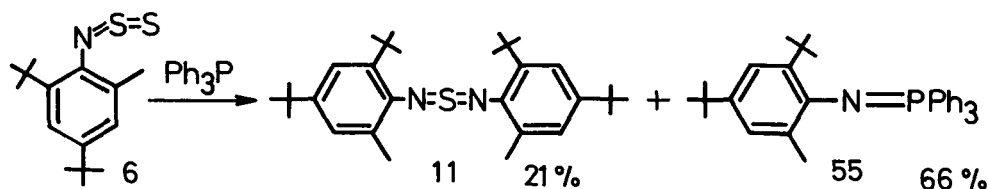
The reaction of **10** with trimethyl phosphite afforded the phosphorimidate (**56**) in 56% yield.
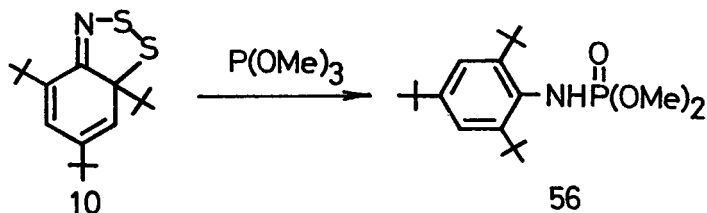
The reactivity of the N-thiosulfinylanilines is in striking contrast to that of N-sulfinyl-anilines, which do not react with trivalent phosphorus compounds; for example, 2,4,6-tri-t-butyl-N-sulfinylaniline (13) reacted with neither triphenylphosphine nor trimethyl phosphite at room temperature.[55a]

When the reaction of 10 with triphenylphosphine was carried out under a stream of oxygen, the sulfur diimide (12) was not produced, but instead the yield of the N-sulfinyl-aniline (13) increased to 39%. Since 10 did not react with oxygen under the reaction conditions, this result suggests that the sulfur diimide (12) and the N-sulfinylaniline (13) were produced via a common intermediate, 2,4,6-tri-t-butylthionitrosobenzene, which could be trapped with oxygen.
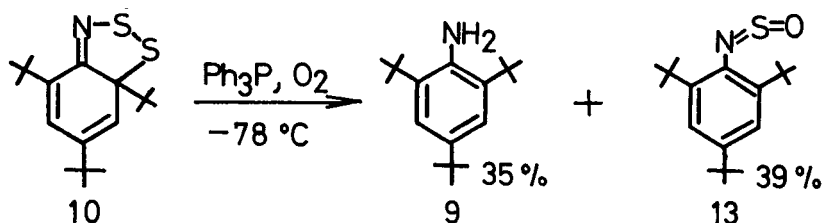

The reactions of sterically hindered nitrosobenzene derivatives (57 and 39) with tri-alkylphosphines afford products which are considered to be formed via nitrenes.[55]
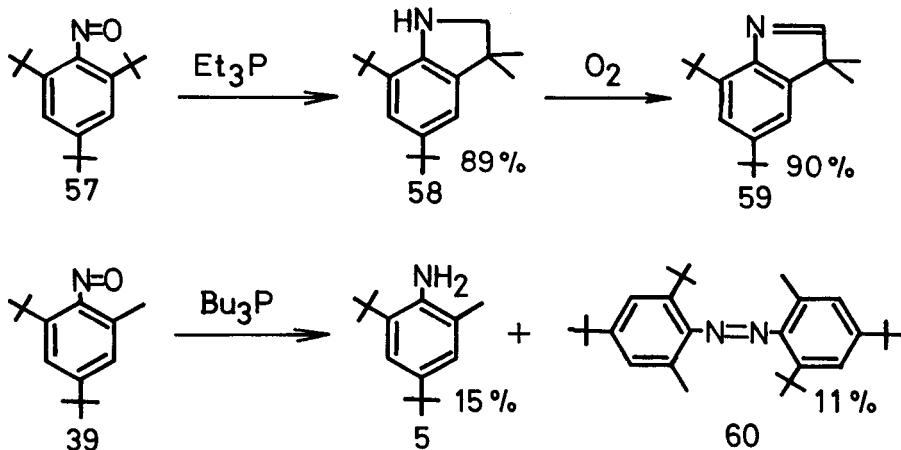
The absence of 59 and 60 in the products of the reaction of 6 and 10 with triphenylphos-phine excludes nitrene formation. Therefore, the probable reaction mechanism can be depicted as in the following Scheme. Nucleophilic attack of triphenylphosphine on 6 or 10 affords the zwitterion 61 which gives the iminophosphorane 62, when R equals methyl. When R equals the more bulky t-butyl, elimination of triphenylphosphine sul-

fide from **61** to give the thionitrosobenzene derivative **63** is a predominant pathway. The thionitroso derivative will then give **65** as described previously. The mechanism of the formation of 2,4,6-tri-*t*-butylaniline (**9**) is not clear, but one possible route is hydrolysis of the zwitterion **61**.
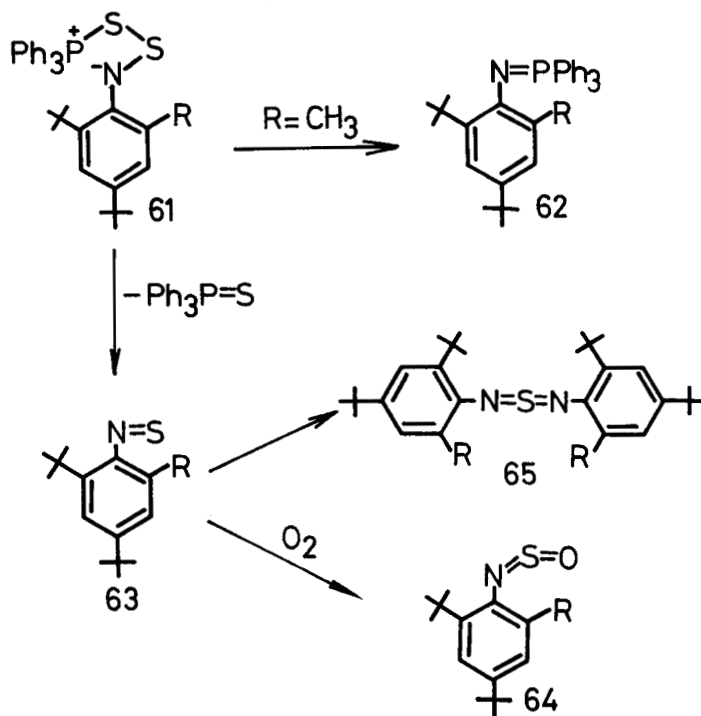
Reaction of **6** with bromine[56] and reaction with *t*-butyl radicals,[57] generated by photolysis of 2,2′-dimethyl-2,2′-azopropane, also gave the sulfur diimide.
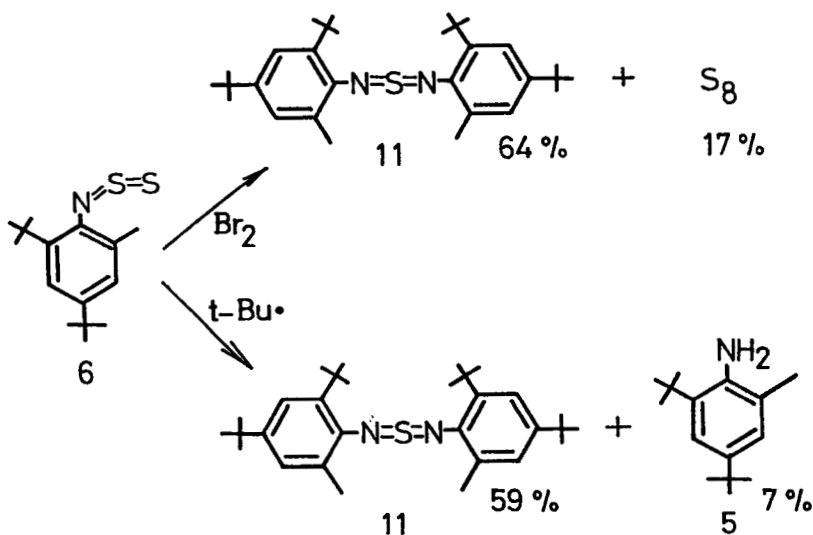
Considering the formation of a sulfur diimide via a thionitroso intermediate as demon-

strated in the reaction of N-thiosulfinylanilines with triphenylphosphine, the reaction mechanism starting with attacks of a bromine or t-butyl radical on the S(II) atom and involving a thionitroso intermediate seems probable.

Ar–N=S=S · Br–Br ⟶ Ar–N=Ṡ–S–Br Br⁻ ⟶ Ar–N=S + SBr$_2$

Ar–N=S=S + t-Bu• ⟶ Ar–N=Ṡ–S-t-Bu ⟶ Ar–N=S + t-BuS•

(4) Reactions with nucleophilic reagents[55]   Nucleophilic reagents attack thiocumulenes, X=S=Y, usually at the S(IV) atom, but attack on X or Y is facilitated as the sum of the electronegativities of X and Y decreases,[1] as in the case of thiocarbonyl S-imides.[58]
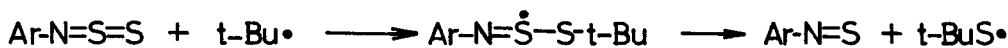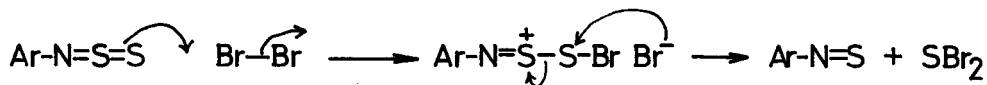
Reactions with Amines.   The sulfinyl group of an N-sulfinylamine has been reported to be transferred to a primary amine.[59]

$$R—N=S=O + R'—NH_2 \longrightarrow R—NH_2 + R'—N=S=O$$

In the case of the N-thiosulfinylaniline **6** reactions with alkylamines afforded the aniline **5** together with some unidentified products. The results are summarized in Table V.

Similarly reduction of **6** to **5** (88%) also took place with thiourea in ethanol.

Reactions with Organometallic Compounds.   Reaction of **6** with an equimolar amount of methylmagnesium iodide afforded the aniline **5** (65%) and the sulfur diimide **11** (9%). In the reaction with an equimolar amount of butyllithium the products were also **5** (54%) and **11** (24%). Reaction of **6** with excess isopropylmagnesium bromide gave 60% of **5**. In contrast to these reactions, the reaction of 2,4,6-tri-t-butyl-N-sulfinylaniline (**13**) with isopropylmagnesium bromide afforded 64% of N-(2,4,6-tri-t-butylphenyl)-1-methylethanesulfinamide (**66**).
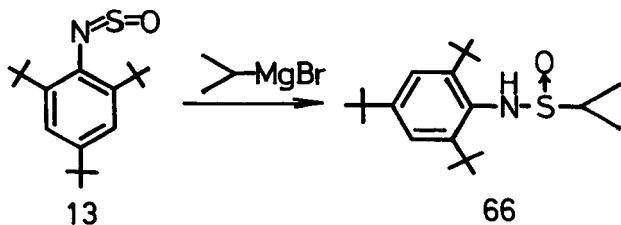
Reaction with an Enamine.   Reaction of **6** with 1-pyrrolidinocyclopentene proceeded rapidly even at −78°C to give the aniline **5** (58%).

Reaction with Hydrogen Sulfide. p-(N,N-Dimethylamino)-N-thiosulfinylaniline (**3**) was reduced by hydrogen sulfide to give N,N-*dimethyl-p*-phenylenediamine which was isolated as its N-benzoyl derivative.[2] Reaction of **6** with hydrogen sulfide in benzene followed by chromatographic treatment on silica gel afforded 51% of the aniline **5**, and another compound which was unstable to chromatographic treatment and decomposed into the aniline **5**.

Judging from the formation of the corresponding reduced compounds in all these reactions it is clear that the N-thiosulfinylamino group has a thiotransfer ability although the detailed reaction mechanism remains to be determined.

TABLE V

Reactions of *N*-Thiosulfinylaniline 6 with Amines

R—NH₂	Reaction Time	Solvent	Molar Ratio R—NH₂/6	Yield of 5 (%)
n-BuNH₂	88 h	EtOH	1.08	41.1
t-BuNH₂	22 h	Et₂O	1.39	30.6
1-AdNH₂[a]	11 days	CH₂Cl₂	1.01	81.1
PhNH₂	7 days	Et₂O	0.94	no reaction
Pyrrolidine	2.5 h	CH₂Cl₂	2.23	63.7

[a] 1-Ad stands for 1-adamantyl.

The conversion of the *N*-thiosulfinylamino group into the amino group can be achieved, of course, with the usual reducing agents. *p*-(*N*,*N*-Dimethylamino)-*N*-thiosulfinylaniline (3) has been reduced with sodium borohydride to give *N*,*N*-dimethyl-*p*-phenylenediamine.[2]

(5) *Reaction with olefins* Thiocumulenes, X=S=Y, are classified into two groups with respect to their behavior towards olefins: one consists of dienophiles and the other of 1,3-dipoles as shown in Table VI.

This difference in reactivity can be related to the electronegativity of the ligands X and Y ($\chi_x + \chi_y$, respectively).[1] Thus, Table VI reveals that the less the value of $\chi_x + \chi_y$, the more enhanced is the 1,3-dipolar nature, rather than the dienophilic nature, of the thiocumulene. Although there has been no report on disulfur monoxide and

TABLE VI

Thiocumulenes Containing Quadrivalent Sulfur

X=S=Y	$\chi_x + \chi_y$	$\chi_x - \chi_y$	Reactivity
O=S=O	7.0	0.0	
N=S=O	6.5	0.5	
C=S=O	6.0	1.5	dienophiles
N=S=N	6.0	0.0	
O=S=S	6.0	1.0	
N=S=S	5.5	0.5	
C=S=N	5.5	0.5	
C=S=C	5.0	0.0	1,3-dipoles
C=S=S	5.0	0.0	

thiocarbonyl *S*-sulfides, it appears reasonable to expect from the value of $\chi_x + \chi_y$ that disulfur monoxide may be a dienophile, whereas a thiocarbonyl *S*-sulfide may be a 1,3-dipole. When $\chi_x > \chi_y$, the larger the difference $\chi_x - \chi_y$ the more reactive is the S═Y bond. Thus, thiocumulenes X═S═O undergo cycloaddition at the X═S bond and unsymmetric sulfur diimides, Ar—N═S═N—SO₂R, undergo cycloaddition at the Ar—N═S bond rather than at that on the electronegative sulfonyl side.[60] Although the borderline between "dienophiles" and "1,3-dipoles" as defined in Table VI is probably too categorical, such a classification is still useful to get a rough idea concerning the properties of S(IV)-cumulenes.

   p-(*N,N*-Dimethylamino)-*N*-thiosulfinylaniline (**3**) gave the cycloadducts **67** and **68** with norbornadiene and cyclopentadiene, respectively, a consequence of its 1,3-dipolar nature.[2]
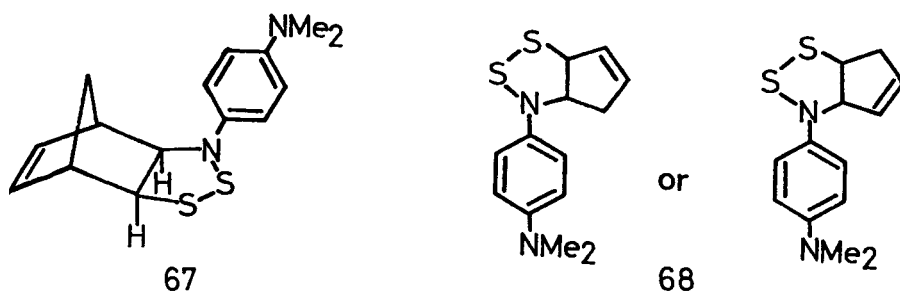

The *N*-thiosulfinylaniline **6** gave the cycloadduct **69** in low yield, but no adduct with dibenzoylacetylene or dimethyl acetylenedicarboxylate.[57]
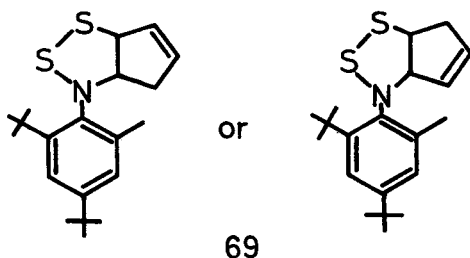
Heating **6** in refluxing 2,3-dimethyl-1,3-butadiene afforded 77% of **5** and 15% of **38**, but no cycloadduct.[57] The much higher ratio of **5** to **38** as compared to that in the thermolysis of **6** in refluxing benzene suggests hydrogen abstraction from the butadiene, most probably by the thionitrosobenzene derivative **49**, and subsequent loss of sulfur, leading to **5**. In this connection it should be noted that recent theoretical calculations predict that simple thionitroso compounds might equilibrate with or even exist in the triplet state.[61]

(6) Other reactions[56]   *p*-(*N,N*-Dimethylamino)-*N*-thiosulfinylaniline (**3**) has been hydrolyzed by successive treatment with hydrochloric acid and aqueous sodium hydrogen carbonate to give *N,N*-dimethyl-*p*-phenylenediamine.[2]

   Reaction of the *N*-thiosulfinylaniline **6** with an equimolar amount of *m*-chloroperbenzoic acid (MCPBA) afforded 2,4-di-*t*-butyl-6-methyl-*N*-sulfinylaniline **70** and aniline **5** in 31 and 41% yields, respectively.
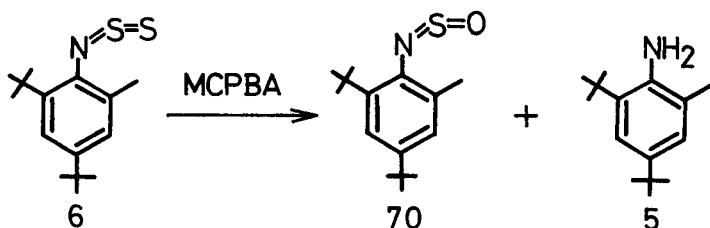
Reaction of MCPBA with the equilibrium mixture **10** gave **71, 50,** and **13.**
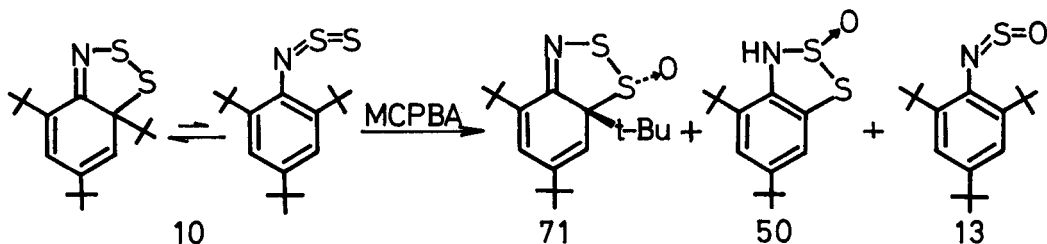
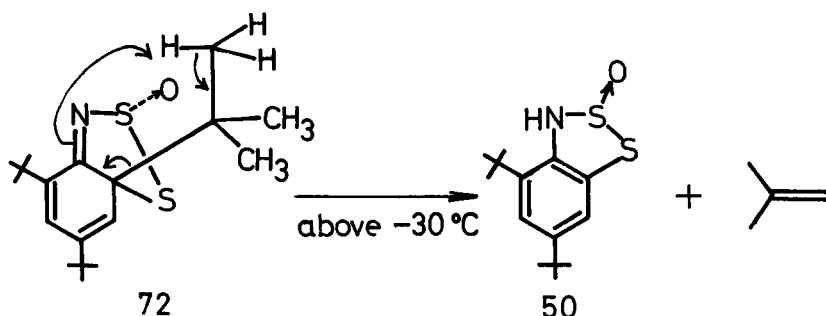The oxide **50** was considered to be produced via the primary product **72** which was found to be stable below −30°C, but to undergo a retroene reaction above that temperature.

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