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Compounds Containing the S═S Bond

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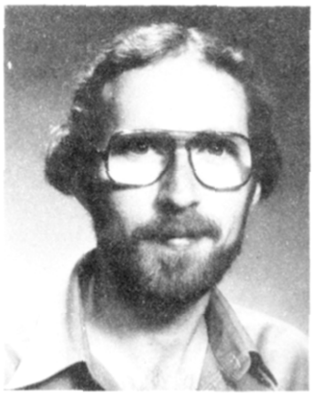
Contents

Gerald Kutney was born in Montreal, Canada, in 1953. He received his B.Sc. from the University of Toronto in 1976 and will be receiving his Ph.D. from the same university in 1982. His graduate work has been associated with the synthesis of novel organosulfur compounds and sulfur-containing natural products. This work was conducted under the supervision of I. W. J. Still of Erindale College *at the University of Toronto. Currently he is working for the* Chemical Research Laboratory of C-I-L Inc. as a research chemist in the pulp and paper group.



Kenneth Turnbull was born in 1951, in Edinburgh, Scotland. He received his B.Sc. and Ph.D. (in 1976) degrees from Heriot-Watt University, Edinburgh. After 2 years as a Postdoctoral Research Associate at the University of Toronto, he joined the chemistry faculty at Grinnell College (Iowa). Since 1981 he has been at Wright State University where he is at present an Assistant Professor. His research interests are in the areas of organosulfur and mesoionic chemistry.

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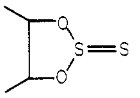
I. Introduction

Compounds containing the S═S bond have long been proposed as intermediates in organic synthesis and, on occasion, as stable entities (see sections VI and VIII). However, as yet, no definitive evidence for the existence of stable thiosulfoxides ($R_2S{=}S$, R = >C) has been forthcoming, although in recent years a number of stable compounds containing the S═S moiety have been prepared (cf. (thiosulfinyl)amines (N═S═S, section VIII), thiono sulfites (I, section VI), and disulfur difluoride (FSSF $\rightleftharpoons$ $F_2S{=}S$, section IV). The inherent instability of the sulfur–sulfur double bond, in contrast to the S═N and S═O bonds of sulfimides and sulfoxides, may arise from the poor p–dπ overlap involved therein.[1]



I

The intriguing problems inherent in the preparation of characterizable thiosulfoxides (and other S═S containing species) have stimulated much research in recent years. Aspects of the controversy relating to the assignment of linear or branched chain structures for di- and polysulfides have been briefly reviewed,[2] but no comprehensive survey has been hitherto available. It is the intention in this review to outline preparative routes and chemical and physical properties of known stable S═S containing compounds and to present evidence both for and against thiosulfoxide intermediacy. Inorganic sulfur branched chain species, except for particularly interesting or illustrative examples, are not included.

Research reports appearing after 1970 have been emphasized with literature coverage extending through December 1981.

II. Background

A. Acyclic Compounds

1. Mustard Gas and Derivatives

The deadly poison, bis(β-chloroethyl) sulfide (mustard gas[3]) (1), was originally prepared by the reaction of bis(β-hydroxyethyl) sulfide with hydrochloric acid.[4]

$$HOCH_2CH_2SCH_2CH_2OH + HCl \rightarrow \underset{\mathbf{1\text{-}7}}{ClCH_2CH_2S_xCH_2CH_2Cl}$$
$$x = 1\text{-}7,\ \text{respectively}$$

The lack of the above reagents in the first World War prompted the Allies to develop an alternative industrial synthesis of 1. This, the Levinstein process, consisted of the reaction of ethylene with disulfur dichloride.[4]

$$CH_2{=}CH_2 + S_2Cl_2 \rightarrow \mathbf{1}$$

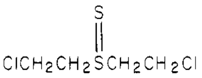
The formation of the sulfide 1, instead of the expected disulfide 2, stimulated the belief that disulfur dichloride existed as an equilibrium mixture,[4]

$$Cl{-}S{-}S{-}Cl \rightleftharpoons Cl{-}S({=}S){-}Cl \rightleftharpoons ClSCl + S$$

Thus, bis(β-chloroethyl) thiosulfoxide (**2b**) was proposed[4] as a possible intermediate in the Levinstein process. The facile loss of a sulfur atom from the disulfide 2 upon heating led Green to postulate[5] that 2 existed in the branched form **2b**. However, Mann, Pope, and Vernon determined that this "product" was actually a mixture of the sulfide 1 and sulfur.[6] Later bis(β-chloroethyl) disulfide was shown, by Bennett[7] and Pernot,[8] to have the nonbranched structure **2a**.

$$ClCH_2CH_2{-}S{-}S{-}CH_2CH_2Cl$$

2a



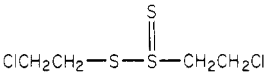
$$ClCH_2CH_2\overset{\overset{S}{\|}}{S}CH_2CH_2Cl$$

2b

Bis(β-chloroethyl) tri- and pentasulfides (3 and 5) were also isolated from the reaction of ethylene with disulfur dichloride.[6] Pernot reported that the trisulfide 3 had the branched structure **3b**,[8] while earlier, Mann, Pope, and Vernon proposed the linear structure **3a**.[6]

$$ClCH_2CH_2{-}S{-}S{-}S{-}CH_2CH_2Cl$$

3a



$$ClCH_2CH_2{-}S{-}\overset{\overset{S}{\|}}{S}{-}CH_2CH_2Cl$$

3b

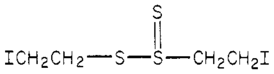
In 1946, Fuson and co-workers concluded that the trisulfide 3 existed in the linear form **3a** since reaction with chlorine yielded the sulfenyl chlorides 8 and 9.[9]

$$\mathbf{3} + Cl_2 \rightarrow \underset{\mathbf{8}}{ClCH_2CH_2SCl} + \underset{\mathbf{9}}{ClCH_2CH_2{-}S{-}S{-}Cl}$$

A preliminary X-ray crystallographic examination of bis(β-iodoethyl) trisulfide (**10**) did not allow distinction between structures **10a–d**,[10] although a later report did eliminate structure **10b**[11] Structural assignment as the linear trisulfide **10a** was confirmed by a later X-ray crystallographic study.[12]

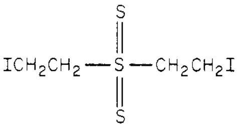
$$ICH_2CH_2{-}S{-}S{-}S{-}CH_2CH_2I$$

10a



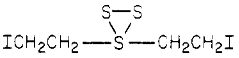
$$ICH_2CH_2{-}S{-}\overset{\overset{S}{\|}}{S}{-}CH_2CH_2I$$

10b



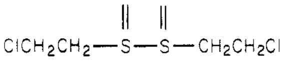
$$ICH_2CH_2{-}\underset{\underset{S}{\|}}{\overset{\overset{S}{\|}}{S}}{-}CH_2CH_2I$$

10c



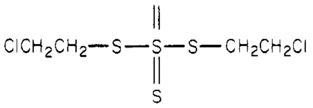
10d

Due to the facile loss of a sulfur atom from both the penta- and heptasulfides 5 and 7 the branched structures **5b** and **7b** have been postulated[9] as likely configurations for 5 and 7, respectively. For similar reasons Macy and co-workers have proposed that bis(β-chloroethyl) tetra- and hexasulfides (4 and 6) exist as the branched species **4b** and **6b**.[4] These compounds have



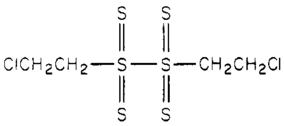
$$ClCH_2CH_2{-}\overset{\overset{S}{\|}}{S}{-}\overset{\overset{S}{\|}}{S}{-}CH_2CH_2Cl$$

4b



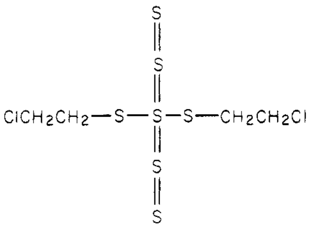
$$ClCH_2CH_2{-}S{-}\underset{\underset{S}{\|}}{\overset{\overset{S}{\|}}{S}}{-}S{-}CH_2CH_2Cl$$

5b



$$ClCH_2CH_2{-}\underset{\underset{S}{\|}}{\overset{\overset{S}{\|}}{S}}{-}\underset{\underset{S}{\|}}{\overset{\overset{S}{\|}}{S}}{-}CH_2CH_2Cl$$

6b

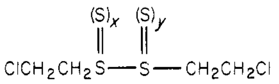


$$ClCH_2CH_2{-}S{-}\underset{\underset{\underset{\underset{S}{\|}}{S}}{\|}}{\overset{\overset{\overset{\overset{S}{\|}}{S}}{\|}}{S}}{-}S{-}CH_2CH_2Cl$$

7b

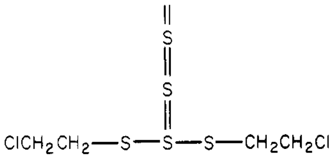
not been rigorously characterized, but structures such as **4b–7b** seem hardly reasonable in the light of current knowledge.

Higher polysulfides of mustard gas (**1**) were considered by Pernot to have the general structure **11a**,[8] while Kinnear and Harley-Mason postulated other unlikely structures such as **11b** and **11c**.[13]

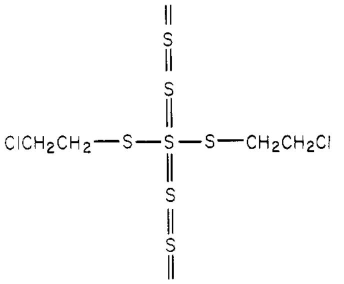


$$ClCH_2CH_2\overset{(S)_x}{\overset{\|}{S}}{-}\overset{(S)_y}{\overset{\|}{S}}{-}CH_2CH_2Cl$$

11a



11b



11c

2. Branched Disulfides and Polysulfides

In 1921 Naik isolated diamino sulfides **13** from the reaction of primary amines with disulfur dichloride.[14] Diamino thiosulfoxides **12** were postulated as intermediates.

$$RNH_2 + S_2Cl_2 \rightarrow \underset{\textbf{12}}{RNH{-}S({=}S){-}NHR} \rightarrow \underset{\textbf{13}}{RNHSNHR}$$

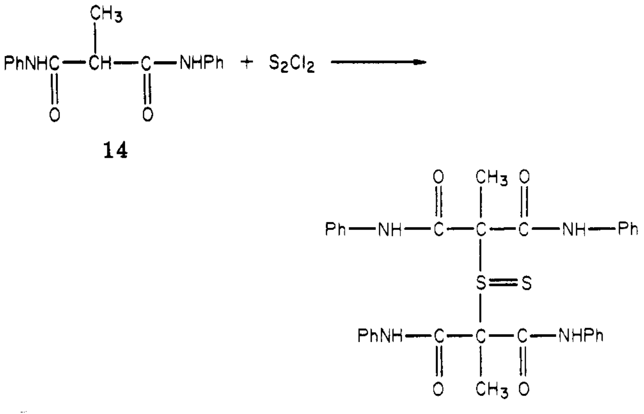
Naik also reported the formation of stable thiosulfoxides **15** and **17** from the reaction of the malondiamides **14** and **16** with disulfur dichloride.[15] With cyanoacetamide (**18**) and disulfur dichloride an unstable compound, proposed to have the thiono structure **19**, was isolated.[16] Naik later demonstrated that products **15** and **17** were in fact the nonbranched disulfides.[17] Thus, **19** may also be a linear disulfide.

Trifluoromethyl disulfide (**20**) appears[18] to exist in the nonbranched form **20a** since reaction with mercuric chloride yields **21**. Compound **22** would be the anticipated product were the thiosulfoxide **20b** to be formed.

$$\underset{\textbf{20a}}{CF_3{-}S{-}S{-}CF_3} + HgCl_2 \rightarrow \underset{\textbf{21}}{CF_3{-}S{-}Hg{-}S{-}CF_3}$$

$$\underset{\textbf{20b}}{CF_3{-}S({=}S){-}CF_3} + HgCl_2 \not\rightarrow \underset{\textbf{22}}{CF_3{-}S{-}Hg{-}CF_3} + HgS$$

Interestingly photolysis of trifluoromethyl disulfide (**20**) yields the corresponding sulfide,[18] possibly via the photoisomerization of the nonbranched disulfide **20a** to the thiosulfoxide (**20b**).[18] X-ray crystallographic,[19] ultraviolet,[20] and infrared[20] spectroscopic studies have further confirmed the linear structure **20a**. X-ray crystallography has also demonstrated that the corresponding trisulfide **23** (R = CF_3) exists in the linear form **23a** (R = CF_3) rather than the branched forms **23b** and **23c** (R = CF_3).[19]



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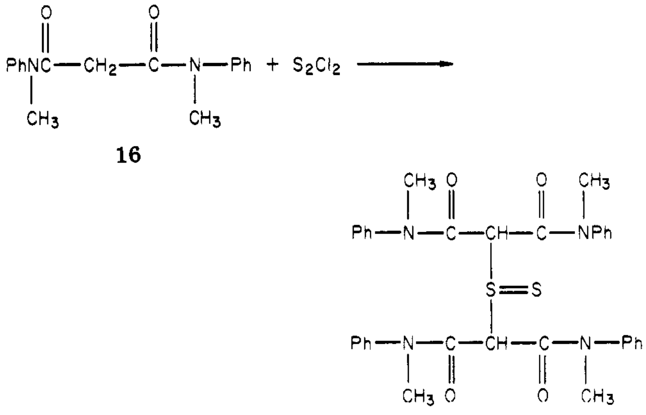
15



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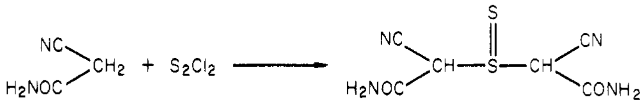
17



18

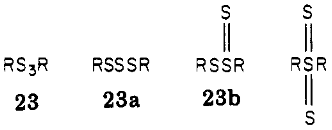
19

In 1903 Wolff and Ott had postulated the formation of the trisulfide **23c** (R = $(MeO_2C)_2CH$) from the reaction of dimethyl malonate with disulfur dichloride and aluminum trichloride.[21] Earlier the nonbranched trisulfide **23a** (R = $(MeCO)_2CH$) had been prepared from the reaction of disulfur dichloride with 2,4-pentanedione.[22] Baer and Carmack could not distinguish

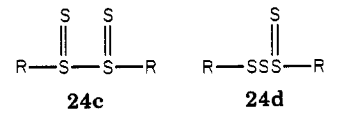
$$MeO_2CCH_2CO_2Me + S_2Cl_2 \xrightarrow{AlCl_3} \textbf{23c},\ R = (MeO_2C)_2CH$$

$$MeCOCH_2COMe + S_2Cl_2 \rightarrow \textbf{23a},\ R = (MeCO)_2CH$$

between the branched (**23b**, **24b**, **24c**) R = $C_{16}H_{33}$) and nonbranched forms (**23a**, **24a**, R = $C_{16}H_{33}$) of di-*n*-hexadecyl tri- and tetrasulfides (**23**, **24**, R = $C_{16}H_{33}$) by



23 **23a** **23b** **23c**



24 **24a** **24b** **24c** **24d**

ultraviolet spectroscopy[23] although the measured dipole moments favored the nonbranched structures (**23a, 24a**, R = $C_{16}H_{33}$).[24] In contrast Bezzi and Lanza reported that the tri- and tetrasulfides **23** and **24** (R = $C_{16}H_{33}$) existed in the branched forms **23b** and **24c** (R = $C_{16}H_{33}$), respectively.[25] In 1917 branched structures **23b** and **24c** had been proposed for some alkali metal polysulfides.[26] Tetrasulfides **24** derived from the reaction of thiolates with disulfur dichloride were reported to

$$RSK + S_2Cl_2 \rightarrow \mathbf{24b}$$

have the branched form **24b** due to the assumed branched nature of disulfur dichloride (see section II).[27] Structures such as **24b** had been proposed by Holmberg in 1908.[28]

Parachor measurements[29] and chemical studies[30] supported the branched structure **24b** (R = C_2H_5) for diethyl tetrasulfide (**24**, R = C_2H_5), while diethyl tetrasulfide prepared from diethyl disulfide and S_2 was proposed to have the structure **24c** (R = C_2H_5).[31] From

$$\text{Et—S—S—Et} + S_2 \rightarrow \mathbf{24c},\ R = C_2H_5$$

radioactive sulfur labelling studies it was concluded[32] that no distinction between the branched (**24b, 24d**) and linear (**24a**) forms of diethyl tetrasulfide was possible. The reactions of ethanethiol with disulfur dichloride and ethyl iodide with sodium tetrasulfide yielded diethyl tetrasulfide (**24**, R = C_2H_5), which Farmer and Shipley stated may or may not be branched.[33] Bloomfield, however, concluded that tetrasulfides (cf. **24**) must be nonbranched (cf. **24a**) when prepared from disulfur dichloride, since disulfur dichloride is nonbranched.[34] In the late 1930s electron diffraction studies[35,36] confirmed the nonbranched structure **24a** for tetrasulfides. This was further substantiated by dipole moment measurements[37] and recently by microwave spectroscopy.[38] Diamagnetic susceptibility measurements for di-*n*-butyl tetrasulfide (**24**, R = C_4H_9), prepared from *n*-butanethiol and disulfur dichloride, supported the nonbranched formulation (**24a**, R = C_4H_9).[39,40]

$$n\text{-BuSH} + S_2Cl_2 \rightarrow \mathbf{24a},\ R = C_4H_9$$

TABLE I: RS_xR

R	x	properties
H	2	electron diffraction[35]
Cl	2	electron diffraction,[35,36] dipole moment,[37] parachor,[45] dielectric constant,[45] Raman,[45] microwave[38]
CH_3	2	electron diffraction,[35] dipole moment,[46] Raman[47]
	3	electron diffraction,[48] dipole moment,[46] Raman[49]
CF_3	2	electron diffraction,[19] IR,[20] UV[20]
	3	electron diffraction[19]
C_2H_5	2	dipole moment,[46] parachor,[29] Raman,[49] diamagnetism[50]
	3	parachor,[29] Raman[49]
	4	parachor,[29] viscosity,[44] atomic refraction[44]
C_3H_7	2	dipole moment,[46] diamagnetism[50]
C_4H_9	2	diamagnetism[39,40]
	3	diamagnetism[39,40]
	4	diamagnetism,[39,40] atomic refraction,[44] viscosity[44]
C_6H_5	4	UV[51]
$C_6H_5SO_2$	3	X-ray[10]
C_6H_{13}	6	UV[51]
C_8H_{17}	2	diamagnetism[40]
	3	diamagnetism[40]
	4	diamagnetism,[40] viscosity,[44] atomic refraction[44]
$C_{16}H_{33}$	2	dipole moment,[24] UV[23]
	3	dipole moment,[24] UV[23]
	4	dipole moment,[24] UV[23]

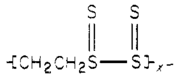
On the basis of an X-ray crystallographic study, Katz proposed that the polymeric tetrasulfide **25** existed in the branched form **25b**.[41] Chemical evidence also supported this conclusion.[42]

$-[CH_2CH_2S_4]_x-$

25

$-[CH_2CH_2SSSS]_x-$

25a



$-[CH_2CH_2\overset{S}{\overset{\|}{S}}\text{—}\overset{S}{\overset{\|}{S}}]_x-$

25b

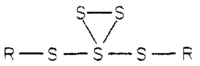
However, in 1960, Schotte and Bergson indicated that these results could be better interpreted on the basis of a linear structure **25a**.[2e] In 1929 Levi and Baroni prepared diethyl pentasulfide (**26**, R = C_2H_5) from ethanethiol, disulfur dichloride, and sulfur.

RS_5R

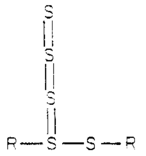
26

RSSSSSR

26a



26b



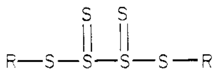
$R\text{—}\overset{S}{\overset{\|}{\overset{S}{\overset{\|}{S}}}}\text{—}S\text{—}R$

26c

Surprisingly, two isomers (**26b** and **26c**, R = C_2H_5) appeared to have been isolated.[31] Structure **26b** was supported by parachor measurements[29] and by chemical studies.[30] Feher, however, suggested that the formation of the two isomers was probably due to impurities.[43] In 1935 Bezzi reported that the results of atomic refraction and viscosity measurements for tri- (**23**), tetra- (**24**), penta- (**26**), and hexasulfides (**27**) "excluded the possibility of formulas with all the sulfur atoms in a chain."[44]

RS_6R

27



$R\text{—}S\text{—}\overset{S}{\overset{\|}{S}}\text{—}\overset{S}{\overset{\|}{S}}\text{—}S\text{—}R$

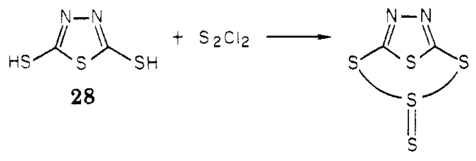
27b

Possible structures such as **23b, 24b, 26b**, and **27b** were also discussed, although no conclusive evidence, in favor of any one representation was presented.

Electron diffraction and other physical measurements for various di- and polysulfides (Table I) have generally confirmed their nonbranched nature, although contrasting reports have appeared.

B. Cyclic Compounds

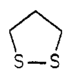
In 1923 Chakravarti reported that the reaction of the dithiol **28** with disulfur dichloride produced the cyclic branched tetrasulfide **29**.[27] The recorded properties[52] for **29** suggest that the compound is actually a polymer.



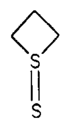
28

29

A branched structure (**30b**) was excluded[53] for the dithiolane **30** on the basis of its stability to reduction by sodium borohydride and its recovery unchanged after reduction by zinc in dilute acid and subsequent reoxidation with iodine.

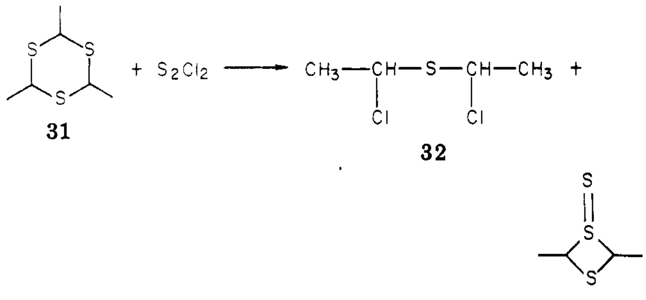


30a



30b

Mann and Pope investigated the reaction of 2,4,6-trimethyl-1,3,5-trithiane (**31**) with disulfur dichloride.[54]



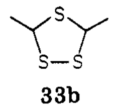
31

32

33a

In addition to the major product, bis(α-chloroethyl) sulfide (**32**), a pale green liquid was isolated which was assigned the branched structure: 2,4-dimethyl-1,3-dithietane 1-sulfide (**33a**).

The latter could be formulated as the isomeric 3,5-dimethyl-1,2,4-trithiolane (**33b**) although the low boiling



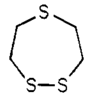
33b

point and green coloration, possibly sulfur contamination, are contrary to the properties expected[52] for such a compound.

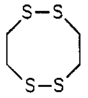
Westlake and co-workers reported[55] that the reaction of ethylene with sulfur gave two compounds with empirical formulas $C_4H_8S_3$ and $(C_2H_4S_3)_4$, respectively.

$$CH_2{=}CH_2 + S_8 \rightarrow C_4H_8S_3 + (C_2H_4S_3)_4$$

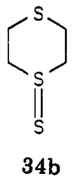
The 1,2,5-trithiepane (**34a**) or 1,4-dithiane 1-sulfide (**34b**) structures were proposed[55] as possibilities for the $C_4H_8S_3$ formulation. Due to the presence of a labile sulfur atom the thiosulfoxide structure **34b** was favored. The other isolated compound, $(C_2H_4S_3)_4$, was ascribed[55] the unusual, highly unlikely, structure **37**. This reaction merits further study.



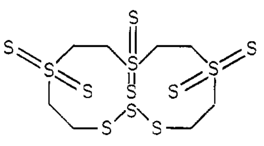
34a



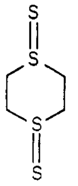
35a



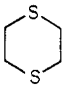
34b



37



35b



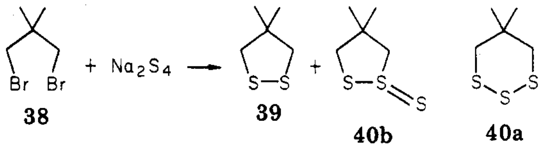
36

Earlier Kaufmann reaction sodium disulfide with 1,2-dichloroethane in an attempt to prepare 1,2,5,6-tetrathiacyclooctane (**35a**).[56] The isolated product was

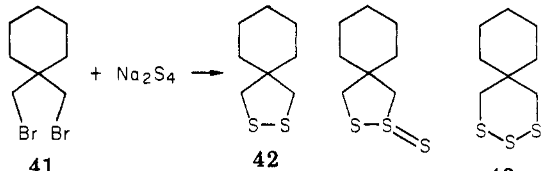
$$ClCH_2CH_2Cl + Na_2S_2 \rightarrow \mathbf{36}$$

not **35a** but 1,4-dithiane (**36**), which was postulated[56] as arising from the, presumably, unstable 1,4-dithiane 1,4-disulfide (**35b**).

In 1938 Backer and Tamsma reported the formation of 4,4-dimethyl-1,2-dithiolane (**39**) and 4,4-dimethyl-1,2-dithiolane 1-sulfide (**40b**) from the reaction of 2,2-dimethyl-1,3-dibromopropane (**38**) with sodium tetrasulfide.[57] Reaction of the dihalide (**38**) with sodium or potassium disulfide produced mainly the dithiolane (**39**) with the putative thiosulfoxide (**40b**) as a minor product. The dibromide **41** was reported to form the 1,2-dithiolane **42** and the branched trisulfide **43b** under similar conditions.[57] The branched forms **40b** and **43b** were favored over the, apparently, more likely 5,5-dimethyl-1,2,3-trithiane (**40a**) and the spiro-1,2,3-trithiane **43a** structures on account of the facile loss of sulfur to form the 1,2-dithiolanes **39** and **42** when **40** and **43**, respectively, were heated in the presence of copper. ^{13}C and ^1H NMR should permit distinction between the branched and linear structures.

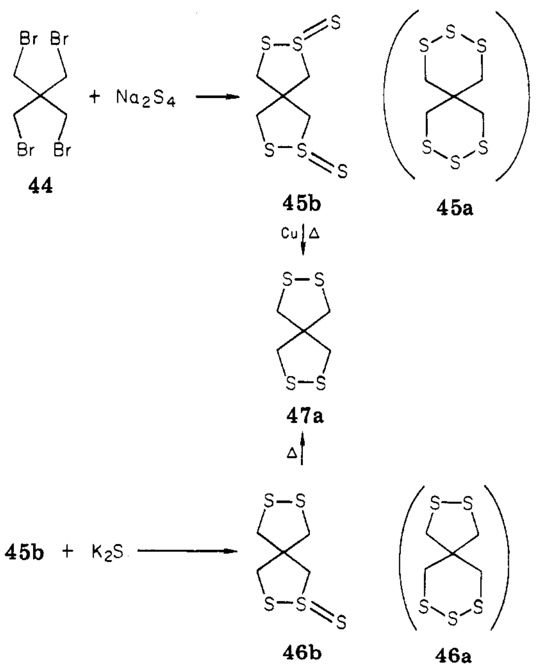


38 39 40b 40a



41 42 43b 43a

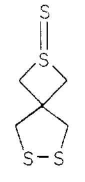
Earlier Backer and Evenhuis isolated a compound, corresponding to the empirical formula $C_5H_8S_6$, from the reaction of pentaerythrityl tetrabromide (**44**) with sodium tetrasulfide.[58] Again due to the facile loss of sulfur, in this case two atoms thereof, on heating the compound in the presence of copper, a dithiosulfoxide structure (**45b**) was proposed instead of the spiro-trithiane formulation (**45a**). Reaction of the compound **45b** with potassium sulfide resulted in the loss of one sulfur atom and a product, postulated to be 2,3,7,8-tetrathiaspiro[4.4]nonane 2-sulfide (**46b**), was isolated.



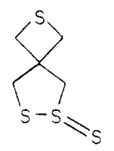
44 45b 45a 47a 46b 46a

The branched structure, instead of the isomeric, 2,3,7,8,9-pentathiaspiro[4.5]decane (**46a**), was again assigned on account of the ready loss of sulfur on heating. The thermal product was the same dithiolane (47a) as had been isolated from the thermolysis of **45b** in the presence of copper.

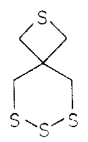
The reaction of the tetrabromide 44 with sodium disulfide produced a solid of empirical formula $C_5H_8S_4$.[58] Structures **47a,b** and **48a,b** were proposed[58] as likely formulations for this product.



47b

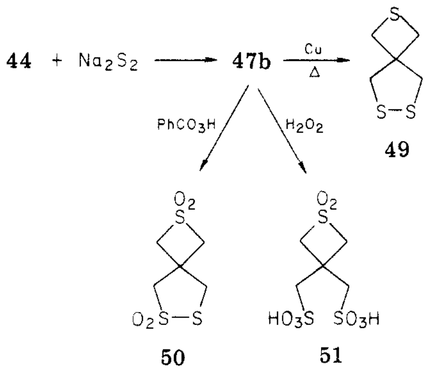


48b



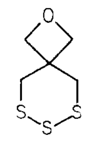
48a

Structure **47a** was eliminated because, unlike 2,3,7,8-tetrathiaspiro[4.4]nonane (**47a**), prepared by the thermolysis of **45**, the new product lost sulfur, upon heating in the presence of copper metal, to produce 2,6,7-trithiaspiro[3.4]octane (**49**).[58] The loss of sulfur, and the unlikelihood that sodium disulfide would add one or three sulfur atoms, caused Backer to eliminate structures and **48a** and **48b**.[58] Furthermore the oxidation of 47b with perbenzoic acid or hydrogen peroxide to produce the disulfone **50** or the thietane 1,1-dioxide **51**, respectively, was cited[58] as conclusive evidence for the branched formulation **47b**.

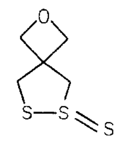


Foss noted that the trithiane structures **40a**, **43a**, **45a**, **46a**, and **48a** would exhibit the same chemical properties as reported for the claimed thiosulfoxides.[2a] Thus, in his view, **40b**, **43b**, **45b**, **46b**, and **47b** should be formulated as **40a**, **43a**, **45a**, **46a**, and **48a**, respectively. The results of ultraviolet and infrared spectroscopic studies for **40b**, **45b**, and **47b** and polarographic studies on **40b** and **47b** supported[59] this hypothesis. The presumed branched sulfides prepared by Backer and coworkers[57,58] did not absorb at 350 µm in the ultraviolet spectrum, in accord with their postulation as 1,2-dithiolanes. Recently Höfle and Baldwin claimed[60] that structure **47b** is inconsistent with the observed nuclear magnetic resonance spectrum and that structure **48a** is the correct formulation. However details of this inconsistency were not reported, nor was it apparent which observations would allow one to differentiate between structures **47b** and **48a**.

Interestingly Campbell has reported the formation of 2,6,7,8-oxatrithiaspiro[3.5]nonane (**52a**), which could not, in his opinion, be differentiated from the branched structure **52b**.[61] Structural differentiation should now be possible via ^1H and ^{13}C NMR spectroscopy.

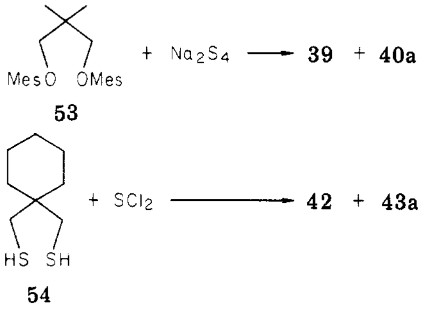


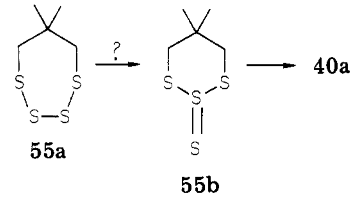
52a



52b

Recently Goor and Anteunis reported the synthesis of polysulfides **39**, **40a**, **42**, and **43a**.[62] 4,4-Dimethyl-1,2-dithiolane (**39**) and 5,5-dimethyl-1,2,3-trithiane (**40a**) were prepared by the reaction of sodium tetrasulfide with the dimesylate **53** whereas the reaction of the dimercaptan **54** with sulfur dichloride was the method of choice for the preparation of **42** and **43a**.[62] The latter synthesis leaves little doubt as to the linear nature of the polysulfide formed. The synthesis of the trithiane **40a**, from the reaction of **53** with sodium tetrasulfide, can be rationalized in terms of initial 6,6-dimethyl-1,2,3,4-tetrathiepane (**55a**) formation, subsequent isomerization to the branched form **55b** and, finally, loss of sulfur from the unstable thiosulfoxide **55b**.

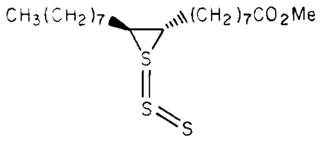




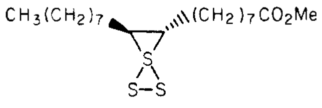
The trithiane structures **39a**, **43a**, **45a**, **46a**, **48a**, and **53a**, as suggested by Foss,[2a] would seem to be correct although, as yet, conclusive evidence has not been forthcoming. Elimination of sulfur by the heating of 1,2,3-trithianes in the presence of copper may involve isomerization of compounds such as **48a** to the branched structure (cf. **48b**).

This labile nature of a sulfur atom in certain polysulfides coupled with the formation of sulfides from reactions with disulfur dichloride or sodium disulfide led early workers to postulate branched chain sulfur compounds. The initial physical and chemical data were conflicting, and it was not until the late 1940s and early 1950s that the generality of nonbranched sulfur chains was widely accepted.

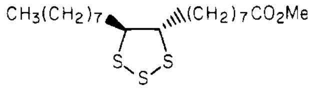
Occasionally even today the preparation of stable species containing S=S bonding is claimed. For example, the reaction of sulfur with methyl oleate or methyl oleidate at 140–160 °C reportedly[63] gives the trans-epithiostearates **56** and **57**, the structures of which were determined by NMR and mass spectrosocpy and the results of chemical transformation (desulfurization and $LiAlH_4$ reduction). In light of the previously amassed evidence in favor of linear structures it seems more than likely that the compounds actually have



56



57



58

trithiolane type structures (cf. **58**).

It is highly unlikely that any of the reported "stable" thiosulfoxide containing compounds actually exist in the branched form. However there are many compounds whose structural assignments remain inconclusive due to the lack of, or conflicting, data concerning them. Modern techniques, especially NMR spectroscopy, should clarify the situation for most, if not all, of these.

III. Inorganic Compounds

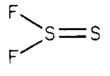
A comprehensive survey of the field of inorganic thiosulfoxides is beyond the scope of this review. The properties of several inorganic species proposed to contain an S=S bond, viz. S_2,[64] S_3,[65], S_4,[66] S_4^{2-},[66] S_2Cl_2,[67] S_2Br_2,[67b] S_2F_2,[68] S_2ClF,[68a] S_2O,[69] $(^-O_3S)_2S_2$,[70] have been described, and reports of branching in inorganic sulfur containing polymers have also appeared.[71]

IV. Equilibrium between Straight and Branched Sulfur Chains

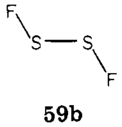
Historically there has been much speculation as to the existence of an equilibrium between the linear (RSS) and branched forms (RS(=S)) in polysulfides.

A. Sulfur Halides

The isolation and identification of the two isomers of disulfur difluoride (**59**)[68b-d] reopened the controversy



59a

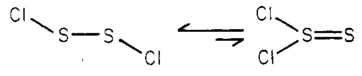


59b

as to whether or not disulfur dichloride (ClS_2Cl) existed as a similar equilibrium mixture.[72]

Electron diffraction[36] and dipole moment[37] measurements indicated that disulfur dichloride possessed the linear structure, whereas some of its chemical reactions suggested that the branched-chain isomer ($Cl_2S{=}S$) was, at least, in equilibrium with the linear form[73] (see section II).

Recently physical measurements[67] have provided evidence for tautomerism (**60** → **61**) in the case of disulfur dichloride. Ultraviolet photolysis of disulfur dichloride, in argon and nitrogen matrices deposited at 12–20 K, followed by infrared spectral analysis of the photolysed matrices indicated the presence of an unstable product assigned the branched structure **61**.[67a] Similar results were obtained, by Feuerhahn and Vahl,[67b] for both disulfur dichloride and dibromide. This was the first definitive evidence consistent with a tautomerism to the branched form of disulfur dibromide, although mass spectral evidence has further indicated it.[74]



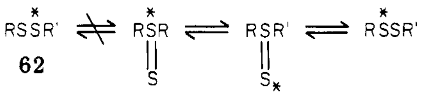
60 **61**

More evidence for the branched chain isomer **61** was obtained recently[67c] by examination of the microwave spectrum of disulfur dichloride. The S–S bond length in S_2Cl_2 was shown[67c] to be shorter than the standard single bond length but not as short as that in S_2F_2.

B. Di- and Polysulfides

The possible equilibrium between linear and branched forms of disulfides has been reviewed briefly.[2d,75] However only acyl and vinylogous acyl disulfides[76] react with triphenylphosphine whereas trisulfides readily form disulfides with the same reagent, possibly via thiosulfoxide intermediacy.[77,78] Desulfurization reactions of di- and polysulfides (RSX, X = $SR^{76,79a-e}$ and $SS_xR^{77,79e-l}$), with trivalent phosphorus reagents, have been extensively studied. Ionic mechanisms involving phosphonium salt intermediates have generally been proposed for such reactions although recently Harpp et al.[78] have suggested that in low polarity solvents desulfurization via thiosulfoxide intermediates may become important.

Wieland and Schwahn demonstrated that reduction of disulfides, prepared from an ^{35}S-labeled thiol and a different unlabeled thiol, did not give two equally radioactive thiols.[80] This observation precluded an equilibrium between the linear disulfide **62** and its branched isomer **63**.



$$\underset{\mathbf{62}}{RS\overset{*}{S}R'} \;\not\rightleftharpoons\; \underset{\underset{\textstyle S}{\|}}{R\overset{*}{S}R} \rightleftharpoons \underset{\underset{\textstyle S_*}{\|}}{RSR'} \rightleftharpoons RS\overset{*}{S}R'$$

63

Irradiation of bis(trifluoromethyl) disulfide (**20a**) in a silica vessel gave bis(trifluoromethyl) sulfide (**64**) and

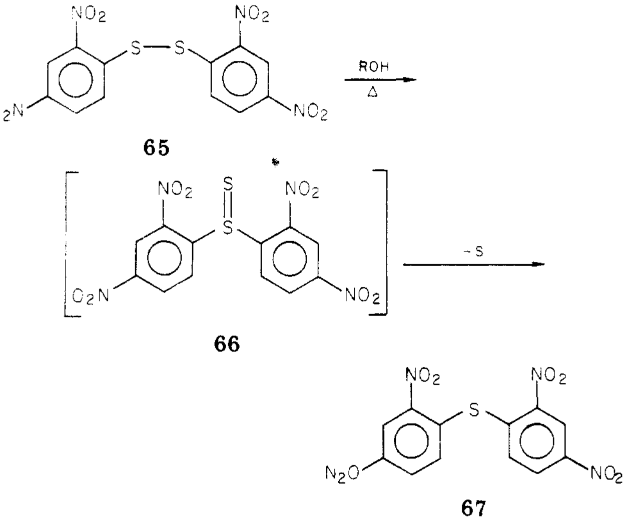
$$\underset{\mathbf{20a}}{CF_3SSCF_3} \rightleftharpoons \underset{\mathbf{20b}}{CF_3{-}S({=}S){-}CF_3} \rightarrow \underset{\mathbf{64}}{CF_3SCF_3} + {}^1/_8S_8$$

sulfur, possibly via thiosulfoxide **20b** intermediacy.[81] Initial radical S–S bond cleavage is more likely, however.

More recently, evidence was amassed for branched sulfur chains (S–S(=S)-S) at low temperatures.[71a,82] Bands in the region of 670 cm^{-1} were observed in the infrared spectrum of the matrix-isolated (noble gases, nitrogen, or carbon disulfide) condensate obtained by cooling sulfur vapor to below −150 °C.[71a,82] Such bands had been attributed to the presence of S_2,[83] but the present evidence[71a,82] suggests that the S=S bond of branched sulfur chains is responsible.

Thiosulfoxide intermediate (**66**) has been proposed[84] for the facile transformation (3 h, boiling ROH) of bis(2,4-dinitrophenyl) disulfide (**65**) to the sulfide

(67).[85a] It is feasible that the withdrawing effect of the 2,4-dinitrophenyl group permits isomerization to the branched form (see sections IV and VI) but does not render 66 stable under these conditions. Thiosulfoxide intermediacy (66) was first proposed for the oxidation of 65 with concentrated HNO_3,[86] but later studies demonstrated that the disulfide (65) used was a mixture of 65 and 67. A reinvestigation by Stepanov and coworkers[85] led them to conclude (from product distribution) that an equilibrium existed between the linear (65) and branched (66) forms.



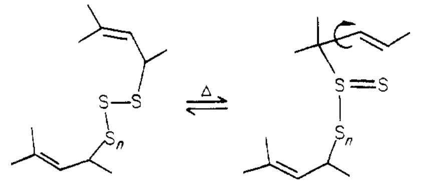
65

66

67

C. Allylic Di- and Polysulfides

The facile cis–trans double bond isomerization of allylically unsaturated *di-* and polysulfides 68 has been rationalized in terms of a thermal equilibrium between 68 and the thiosulfoxide 69.[87] Rotation around the indicated bond in 69 can then explain the rapid interconversion of meso and racemic forms of 68b. The isomerization (68b, one pure isomer to a 50:50 mixture of both) was observed to proceed at a much faster rate than homolytic S–S bond exchange and disproportionation reactions, and the rate was unaffected by the presence of tetrasulfides,[87a] which are known[88] to produce RS_2 radicals under similar conditions An intermolecular chain mechanism (involving homolytic S–S bond cleavage) for exchange of trisulfide end groups was similarly discounted from the observation that the rate was independent of concentration and no mixed trisulfides were detected when the isomerization was performed in the presence of another trisulfide.[87a] The invariance of isomerization rate with change in solvent polarity mitigates against charge separation in the transition state. Likewise, homolytic C–H or C–S cleavage can be disregarded in that neither oxygen nor 2,6-di-*tert*-butyl-4-methylphenol affect the rate, and isoallylic compounds (cf. 70) are not formed in the reaction. Preliminary evidence indicates that a similar isomerization occurs for the double bonds in the related di- and trisulfides 71a and 71b, with a rate constant of the same order as that found for the isomer interconversion of 68.[60]

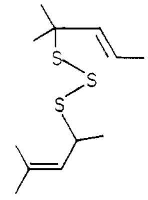


68a, $n = 0$
68b, $n = 1$
68c, $n = 2$

69a, $n = 0$
69b, $n = 1$
69c, $n = 2$

TABLE II

	c	e	d	a	b
k, 10^{-4} s^{-1}	0.70	8.6	8.9	140	190



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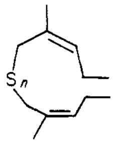
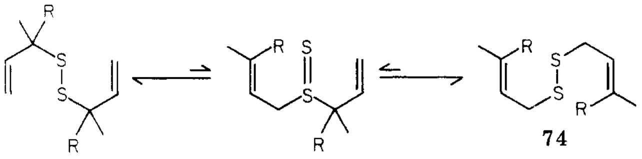


71a, $n = 2$
71b, $n = 3$

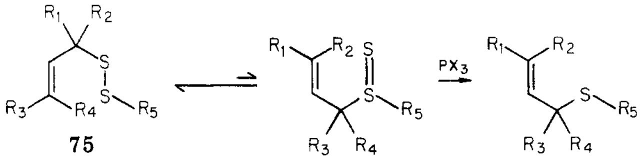
α-Substituted allylic disulfides (72) rearrange at room temperature to the more stable isomers 74 with full double allylic inversion.[60] Contrastingly the alkyl allyl disulfides 75a, 75b are thermally stable. These observations were rationalized in terms of an intramolecular double [2,3]-sigmatropic rearrangement of the diallylic species 72 via the thiosulfoxide 73.



72

73

74



75

76

77

	R_1	R_2	R_3	R_4	R_5
a	H	CH_3	H	H	CH_3
b	CH_3	CH_3	H	H	CH_3
c	H	H	CH_3	CH_3	CH_3
d	H	H	H	H	$CH_2CH{=}CH_2$
e	H	H	H	H	CH_3
f	H	C_6H_5	H	H	CH_3

The rearrangements of 72, (R=H or Me) followed first-order kinetics, and the negative value for $\Delta S^{\ddagger}$ (obtained by NMR spectroscopy) was consistent with a cyclic transition state and similar in magnitude to those values reported for the allylic sulfenate to sulfoxide rearrangement.[89]

Evidence for thiosulfoxide 76 intermediacy was obtained by trapping experiments. Allylic disulfides react rapidly with triphenylphosphine below 100 °C whereas alkyl and aryl disulfides are stable under these conditions.[90] Accordingly it has been proposed that

TABLE III

species	bond dissociation energy, kcal mol^{-1}	heat of formation $\Delta H_f^\circ{}_{298}$, kcal mol^{-1}	entropy, $S^\circ{}_{298}$, cal mol^{-1} K	ref
S_2	102.5	30.7	54.5	92
OS=S	77	−10	63.8	92, 93
F_2S=S	[>57 ± 8][a]	[<−60 ± 6][a] −96 ± 10	70.0	91, 92
Me_2S=S	[53 ± 4][a]	[4 ± 3][a]		91
H_2S=S	[51 ± 7][a]	[10 ± 7][a]		91
MeSSMe[b]	74 ± 2	−5.8	80.5	94
HSSH[b]	66 ± 2	3.8	62.3	94, 95

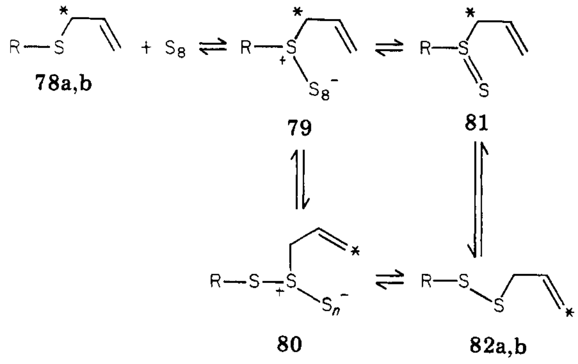
[a] Values in brackets are Benson's estimates.[91] [b] These values are included for comparison purposes.

branched-chain intermediates are involved.[87]

Treatment of the allyl alkyl disulfides **75** with triphenylphosphine was thus anticipated to afford the sulfides **77** and Ph_3P=S via trapping of the intermediate thiosulfoxide **76**. Additionally, increasing the bulk of R_3, R_4, and R_5 should hinder the formation of the thiosulfoxide **76** (and hence **77**), whereas increasing size of R_1 and R_2 should favor thiosulfoxide **78** (and **77**) formation.[60] This was verified experimentally by measurement of the rate of reduction of the allylic disulfides **75a–c** at 60 °C (**75e** and **75f** spontaneously lose sulfur at 25 °C) as shown in Table II.

At high enough concentrations of triphenylphosphine the reaction with **75** is first order with $\Delta H^\ddagger = 20 \pm 1$ kcal and $\Delta S^\ddagger = -9 \pm 1$ eu[60] and, according to Benson,[91] assuming the triphenylphosphine reaction to have an activation energy of 3–4 kcal, the thiosulfoxide must then have a heat of formation no more than 10 kcal greater than that for the disulfide. Table III shows some measured, or estimated, thermodynamic data for various molecules containing the S=S functionality.

Dialkyl sulfides (cf. diethyl and dibenzyl) are apparently inert toward reaction with S_8, even at 90 °C for several days.[96] However, under identical conditions allyl methyl sulfide (**78a**) and diallyl sulfide (**78b**) were converted (ca. 40%) to the corresponding disulfides (**82a**, **82b**) with complete allylic rearrangement (by NMR), as demonstrated by the conversion of allyl-*1,1*-d_2 methyl sulfide to allyl-*3,3*-d_2 methyl disulfide. These results (**78** → **82**) have been interpreted[96] as occurring through a series of equilibria involving dipolar polysulfide chains (cf. **79**, **80**) and thiosulfoxide (**81**) intermediates.



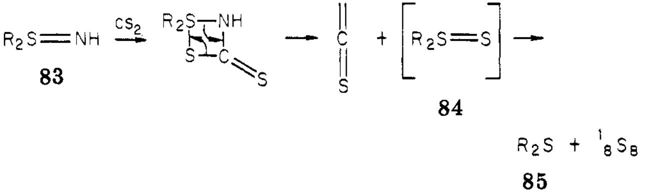
78a,b **79** **81** **80** **82a,b**

a, R = CH_3; b, R = CH_2CH=CH_2

V. Thiosulfoxide Intermediates in the Reactions of Sulfoxides, Sulfimides, Sulfur Ylides, and Thiolsulfinates

The intermediacy of thiosulfoxides in the reduction, by sulfurating agents, of compounds containing semipolar linkages (e.g., sulfoxides, S=O, and sulfimides, S=NR) has been discussed by many workers.[1,97–118]

The reaction of alkyl sulfimides **83** with carbon disulfide, to give sulfides **85** and sulfur, has been proposed[98] to involve the unstable thiosulfoxide intermediates (**84**).



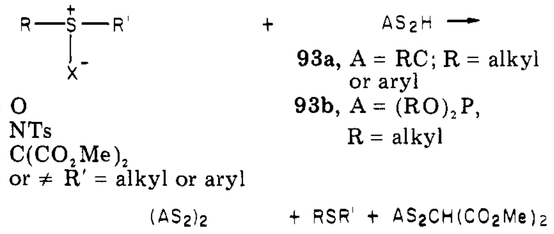
83 **84** **85**

R = Et or Me

In a series of papers the efficacy of sulfoxides (usually Me_2SO) as oxidants for various thio acids (A–SH, A = RC(=O),[99a–c] RC(=S),[99f] R_2P(=O),[99a,b,e] and R_2P(=S)[99b,d,g,h]), thiols (RSH),[100] thiocarbonyl compounds (RC(=S)R′),[101,102c,103] and thiophosphoryl compounds (R_3P=S)[102] was established. The thioacids (A–SH, A = RC(=S) and R_2P(=S)) have been shown to efficiently reduce other semipolar linkages such as sulfimides (R_2S=NR′) and sulfur ylides (R_2S^+—$^-CR'_2$)[99f–h]

Mikolajcyzk[99,101,102] proposed thiosulfoxide intermediates **88**, and **91** in several of the above reactions, and general mechanistic routes to their formation are outlined below (Schemes I and II).

Oae and co-workers also examined the reactions of carbodithioic acids (RCS_2H) (**93a**) and *O,O*-dialkyl dithiophosphates ($(RO)_2PS_2H$) **93b** with sulfoxides (**92a**), sulfimides (R_2S=NTs) (**92b**), and sulfonium ylides ($R_2S\underline{+\ -}C(CO_2Me)_2$) (**92c**).[104] The appropriate



92a, X = O
92b, X = NTs
92c, X = $C(CO_2Me)_2$
R = or ≠ R′ = alkyl or aryl

93a, A = RC; R = alkyl or aryl
93b, A = $(RO)_2P$, R = alkyl

94a, A = RC
94b, A = $(RO)_2P$

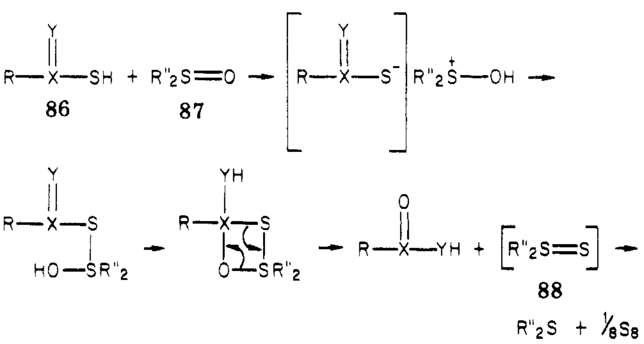
95

96a, A = RC
96b, A = $(RO)_2P$

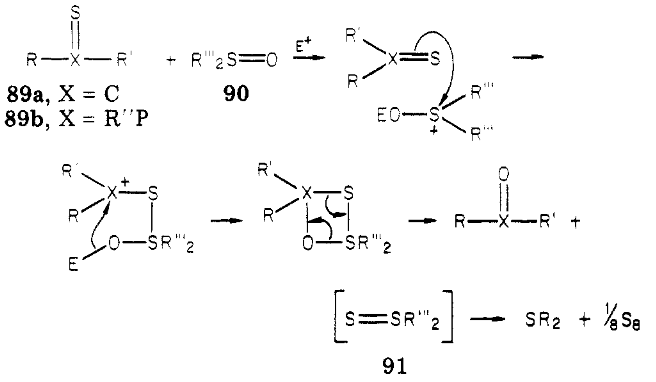
sulfides (cf. **95**) were obtained in each case along with the disulfides **94** (from **92a**,**92b**) and dithio esters **96** (from **92c** only).

Oae rationalized[104] the formation of the disulfides **94** and dithio esters (**96**) in terms of the same intermediate sulfonium salt **97** formed by initial protonation of the

SCHEME I



SCHEME II

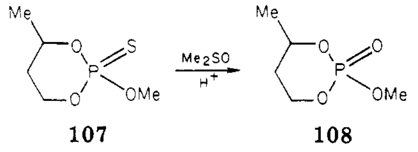


terminal X group (in **92**) by the appropriate dithioic (**93a**) or dithiophosphoric acid (**93b**). Subsequent transformations are shown in Scheme III. Mikolajczyk also isolated disulfides **103** from the reactions of sulfoxides with thiocarboxylic and phosphorus thio and dithio acids.[99a,d] On account of the sensitivity of product distribution (disulfides or sulfur-free acid) to temperature and solvent effects it was proposed that oxidation of the thio and dithio acids with sulfoxides was a bidirectional reaction involving intramolecular (Scheme I) or intermolecular decomposition of the intermediate adduct **101** (Scheme IV).

The importance of the sulfoxonium cation (cf. **97**) was demonstrated by the failure of aryl sulfoxides (compared to the more basic alkyl sulfoxides) to react with diphenylphosphinothioic acid ($R_2P(S)OH$). This was further confirmed by the rate enhancement effected by the addition of strong acids (*p*-toluenesulfonic acid, boron trifluoride, trifluoroacetic acid).[99a,d]

Chiral phosphine sulfides **104** react with dimethyl sulfoxide in the presence of sulfuric acid to give the corresponding phosphine oxides (**106**) with complete inversion of configuration at phosphorus.[102a,b,d] Such a result mitigates against a Wittig-like intermediate (and hence a thiosulfoxide (S═S) intermediate) and suggests[102b,d] an intermolecular decomposition of the initial protonated species **105** (Scheme V).

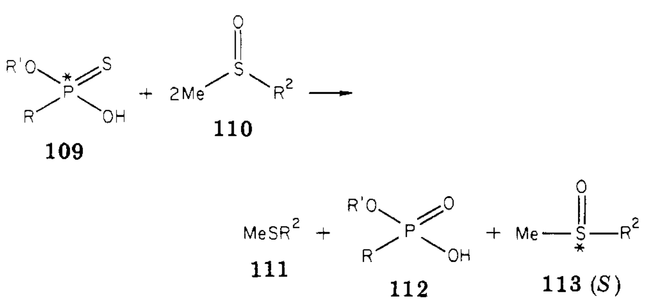
However the reaction of *cis*- and *trans*-dioxaphosphorinan sulfides **107** under similar conditions resulted



a, cis; b, trans

in full retention of configuration at phosphorus.[102a]

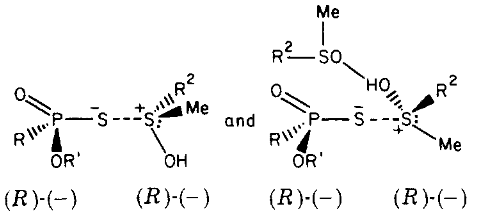
Previously Mikolajczyk and Para[99e] had shown that chiral phosphonothioic acids (**109**) (1 equiv) reacted



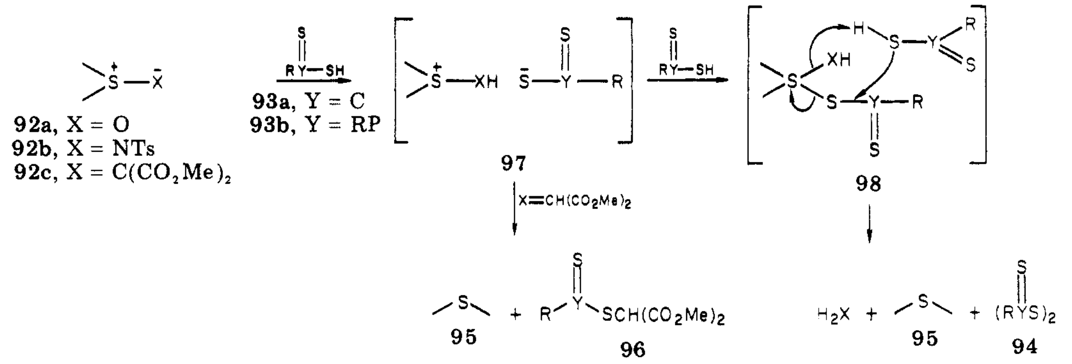
a, R′ = R = ethyl; (*R*)-(−)
b, R′ = *i*-Pr; R = methyl, (*R*)-(−)

with racemic methyl alkyl sulfoxides (**110**) (2 equiv) to give the appropriate methyl alkyl sulfide (**111**), phosphorus oxo acid **112**, and optically active recovered sulfoxide **113**. It appears that the (-)-thio acids **109a** and **109b** both have the *R* configuration and react preferentially with the sulfoxide enantiomer of the same configuration.

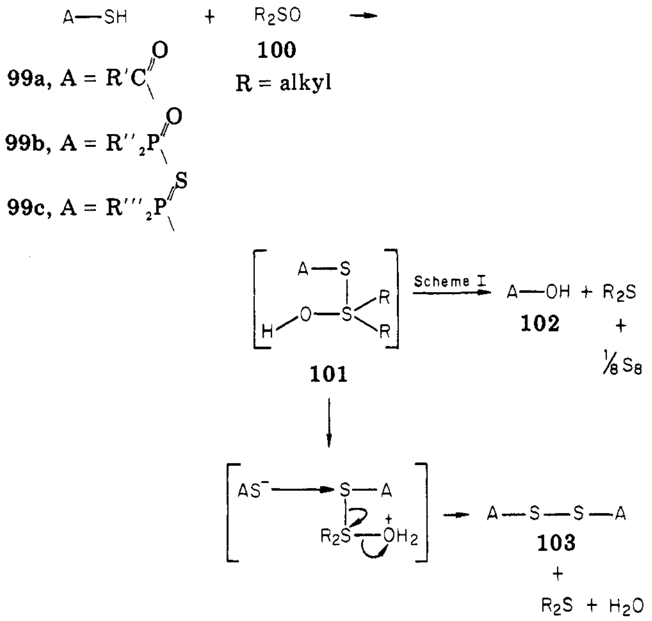
These results were rationalized[99e] on the basis of steric control of asymmetric induction, and the different rate of reduction of the enantiomeric sulfoxides was considered as being due to nonbonding interactions between substituents attached to the phosphorus and sulfur atoms. The favored transition states (en route to a Wittig-type intermediate and subsequent thiosulfoxide S═S) were postulated[99e] as depicted below.



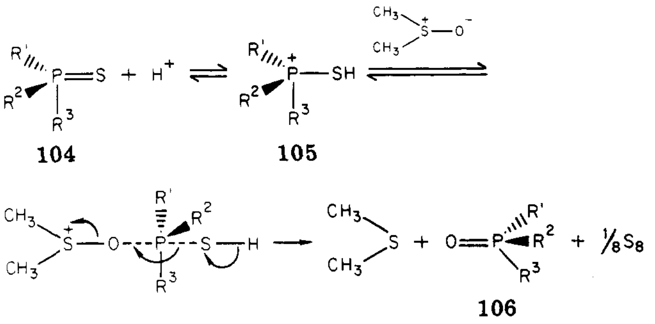
SCHEME III



SCHEME IV

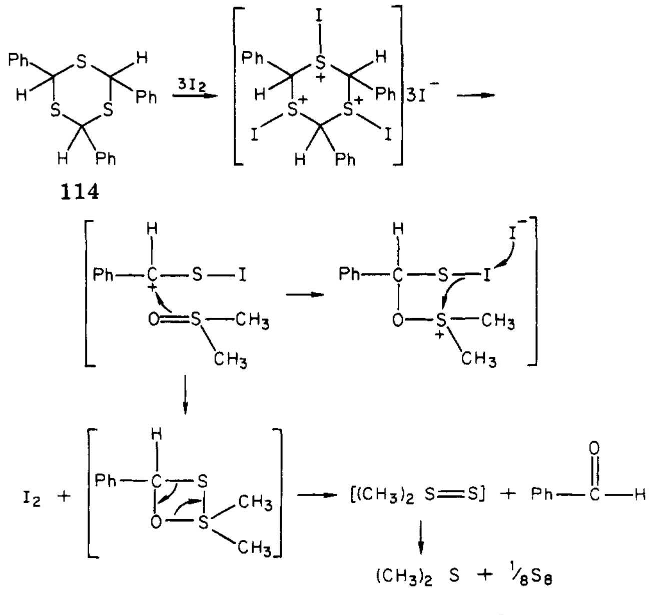


SCHEME V



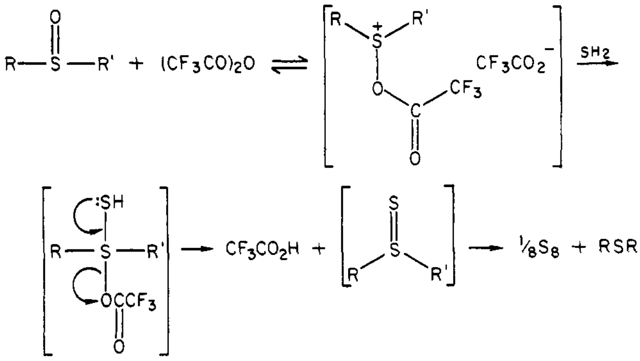
a, R′ = CH_3; R² = n-C_3H_7; R³ = C_6H_5; (*R*)-(+)
b, R′ = CH_3; R² = C_6H_5; R³ = $CH_2C_6H_5$; (*S*)-(−)
c, R′ = CH_3; R² = C_6H_5; R³ = *t*-C_4H_9; (*S*)-(−)
d, R′ = R² = R³ = C_6H_5

SCHEME VI

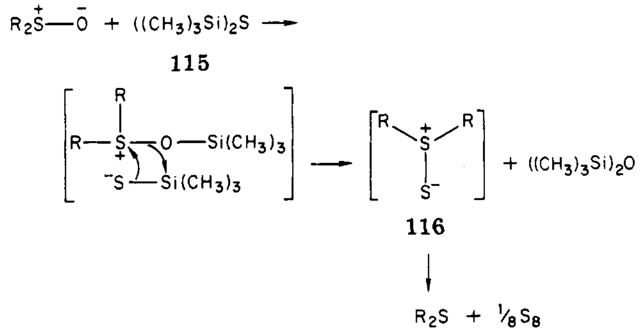


Thiosulfoxides have also been suggested as intermediates in the unusual oxidative desulfurization reactions of *s*-trithianes (cf. **114**) with iodine in dimethyl sulfoxide[105] (Scheme VI).

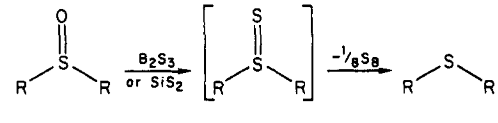
SCHEME VII



SCHEME VIII



SCHEME IX



More recently sulfoxides were reduced to the corresponding sulfides, in high yield, by a trifluoroacetic anhydride–hydrogen sulfide system.[106] The mechanism is unclear, but the first step is apparently nucleophilic attack on the anhydride by the sulfoxide oxygen. This is suggested by the selective reduction of sulfoxides in the presence of sulfinates (RS(═O)OR′) or thiolsulfinates (RS(═O)SBu-*t*), the external oxygen atoms of which are undoubtedly less nucleophilic than that in the sulfoxide. Although thiosulfoxides were not mentioned as potential intermediates in the reaction, a mechanism to their formation can be postulated (Scheme VII).

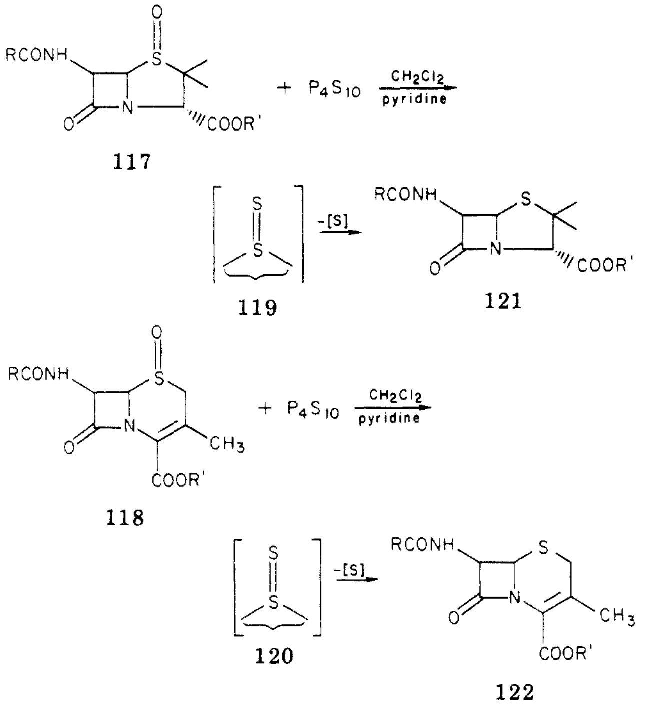
Alkyl and aryl sulfoxides are also reduced, to the corresponding sulfides, by hexamethyldisilthiane (**115**) (or hexamethylcyclotrisilthiane), possibly via thiosulfoxide (**116**) intermediates[107] (Scheme VIII).

Steric and solvent polarity effects lead to the conclusion that nucleophilic attack by sulfoxide oxygen on silicon is the important initial step.[107]

Thiosulfoxides may also be intermediates in the reactions of sulfoxides with boron sulfide (B_2S_3)[1,108,109] and silicon sulfide (SiS_2)[1,109a] (Scheme IX).

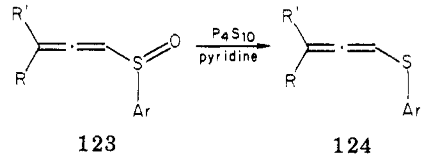
In recent years studies of the reactions of sulfoxides and sulfimides with tetraphosphorus decasulfide (P_4S_{10}) have indicated the likelihood of thiosulfoxide intermediates.[1,109a–118]

In 1976 Micetich showed[110] the efficacy of P_4S_{10} (in the presence of pyridine) as a reductant for conversion of penicillin and cephalosporin sulfoxides **117** and **118** to the corresponding sulfides **121**, and **122** under mild conditions (CH_2Cl_2, 20 °C). Since no precautions were taken to exclude moisture during the reaction, it was



proposed[110] that thiophosphoric acids, formed by reaction of P_4S_{10} with adventitious water, were the active reductants, or, alternatively, that thiosulfoxide intermediates **119** and **120** were initially formed and gave the appropriate sulfides **121** and **122** by subsequent extrusion of sulfur.

The same reducing system (P_4S_{10}, pyridine, CH_2Cl_2) was successfully utilized for the conversion of allenic sulfoxides **123** to the sulfides **124**.[111]



It was later demonstrated[1,109a,112,115] that the effective reduction of other stable alkyl and aryl sulfoxides **125**

$$\underset{\mathbf{125}}{R_2S{=}O} + P_4S_{10} \rightarrow \underset{\mathbf{126}}{[R_2S{=}S]} \rightarrow \underset{\mathbf{127}}{R{-}S{-}R} + {}^1/_8S_8$$

with P_4S_{10} did not require the presence of pyridine, nor did anhydrous conditions affect the product distribution.

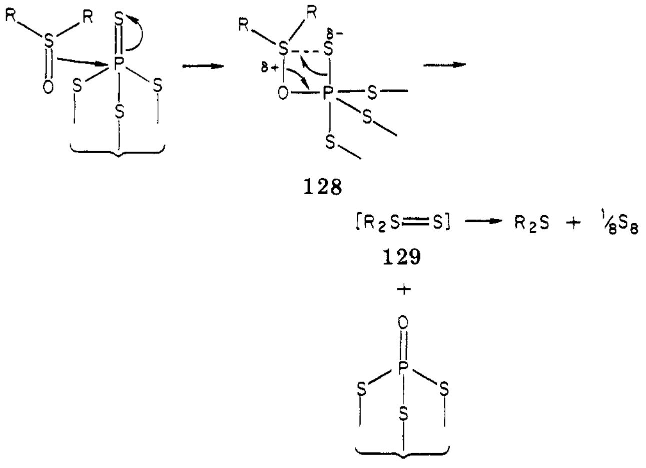
Both methylene chloride[112] and carbon disulfide[1,109a] have been used as solvent media for the reaction, CS_2 apparently allowing reaction to proceed at lower temperatures. No conclusive evidence as to the intermediacy of thiosulfoxides (**126**), in the reaction **125** → **127** has, as yet, been obtained[113] although recently dimethyl disulfide and allyl disulfides were isolated[114] as minor products from the reactions of P_4S_{10} with neat dimethyl sulfoxide[115] and allyl sulfoxides (in CS_2),[109a] respectively. These observations may be readily rationalized in terms of initial thiosulfoxide formation and subsequent isomerization (see section IV).

Good correlation between the rate of reduction and increasing electron-donor capability of X was observed[112] for a series of sulfoxides ((p-$XC_6H_4)_2SO$) (Table IV).

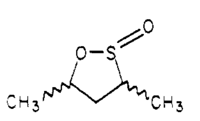
Considering the adamantane-like structure of P_4S_{10}, in the solid state (with four equivalent P=S bonds), these results suggest[112] that an initial attack on phosphorus by the sulfoxide oxygen atom forms a Wittig-like intermediate or transition state (**128**) which breaks down to give an unstable thiosulfoxide **129**.

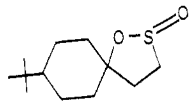
TABLE IV

sulfoxide (p-$XC_6H_4)_2SO$	% conversion to sulfide (CH_2Cl_2, 4 h, 25 °C)
X = NO_2	11
X = Cl	24
X = H	39
X = CH_3	81
X = OCH_3	100

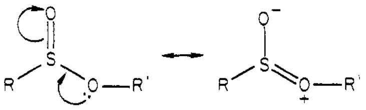


Further support for this initial attack by sulfoxide oxygen was afforded by the observation that sulfones (RSO_2R)[116] and the cyclic sulfinates **130** and **131** did not similarly react with P_4S_{10}.

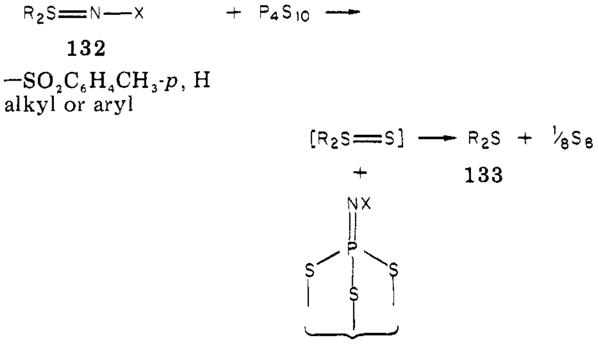

130


131

This suggests that, in **130** and **131**, inductive electron withdrawal by the ring oxygen is more important in determining the nucleophilicity of the external oxygen than is a resonance contribution of the type shown below.



P_4S_{10} was also shown[117] to efficiently reduce sulfimides (cf. **132**) to sulfides **133**. Correlations between the electron-donor abilities of groups attached to the sulfimide sulfur atom and the rate of reduction were



X = $-SO_2C_6H_4CH_3$-p, H
R = alkyl or aryl

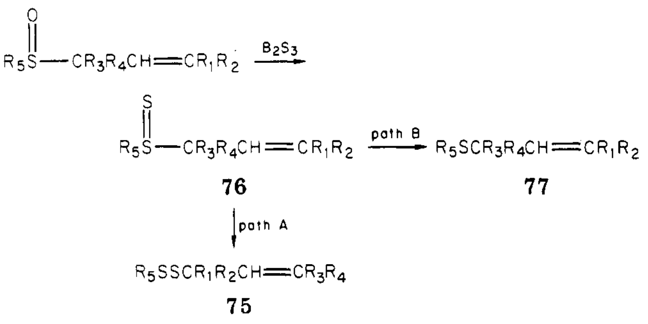
again apparent, and on this basis, it was proposed[117] that a mechanism similar to that postulated for sulfoxide reduction[112] was operative.

Thiosulfoxides may also be involved as intermediates in the reductions of sulfoxides with other phosphorus reagents, viz. the dimer of (*p*-methoxyphenyl)thioxophosphine sulfide[115] and thiophosphoryl bromide (PSBr$_3$).[118] With the former, both dimethyl and tetramethylene sulfoxides (**134a**, **134b**) were converted to their respective sulfides and disulfides[115] (Scheme X).

Thiophosphoryl bromide proved to be, in many ways, a superior reagent to tetraphosphorus decasulfide for the reduction of both alkyl and aryl sulfoxides.[118] The reagent was, in contrast to P$_4$S$_{10}$, conveniently soluble in common solvents, and the yields of sulfides obtained were, in general, greater than those resulting from the reaction of P$_4$S$_{10}$ with the appropriate sulfoxides. The mechanism is unclear at present, but, by analogy with the P$_4$S$_{10}$ reaction,[112] it seems probable[118] that a Wittig-like intermediate is first formed, subsequent breakdown of which affords consecutively a thiosulfoxide and then sulfide (Scheme XI).

Higher yields of allyl disulfides are obtained by treatment of allyl sulfoxides with B$_2$S$_3$ (compared to P$_4$S$_{10}$).[1,109] Baechler[109b] recently employed this reagent for reaction with a series of allyl aryl sulfoxides. Correlation of aryl and allyl structural modifications with disulfide/sulfide product ratio distribution permitted assessment of the factors affecting thiosulfoxide stability. The two competitive paths open to putative intermediate thiosulfoxides, viz., (2,3)-sigmatropic rearrangement to disulfides (path A) (see section IVC) and spontaneous desulfurization to sulfides (path B), appear to be influenced by aryl substituent modifications.

In accord with expectation (viz., that electron-withdrawing groups would stabilize the thiosulfoxide sufficiently (see sections IV and VI and **65** → **67**) to allow sigmatropic rearrangement to compete more effectively with desulfurization) a greater yield of disulfide product was obtained for **75**, R$_5$ = 4-O$_2$NC$_6$H$_4$ (40%), than for **75**, R$_5$ = 4-CH$_3$OC$_6$H$_4$ (0%) (cf. **75**, R$_5$ = C$_6$H$_5$, 30%).



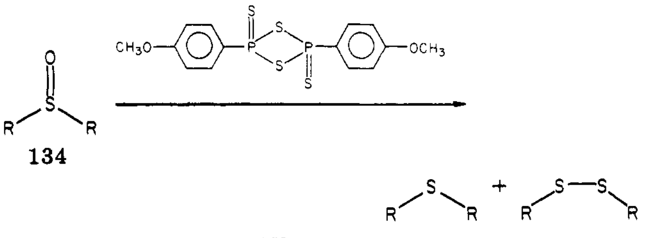
R$_1$ = H; R$_2$ = H, C$_6$H$_5$; R$_3$ = R$_4$ = H; R$_5$ = Ar

These results would argue for (p–d)π, rather than dative, bonding between the thiosulfoxide sulfur atoms,[109b] in agreement with previous conjecture[2a,b] and experimental evidence.[68,121]

A thiosulfoxide has been discussed as a possible intermediate in the acid- or sulfide-catalyzed decomposition of *S*-*tert*-butyl benzenethiosulfinate (**135**) (Scheme XII).[119]

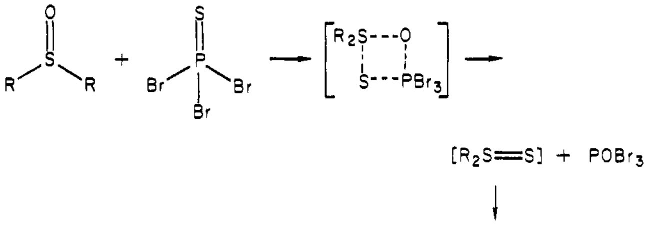
It was suggested[119] that the presumably[109,112] facile breakdown of thiosulfoxides, to give sulfides and sulfur, may release sulfur in a highly reactive form. Insertion into the S–S bond of **135** by this reactive sulfur atom, or direct sulfur transfer from the thiosulfoxide, might generate a species postulated as an intermediate in the mechanistic routes to **138** and **139**.

SCHEME X

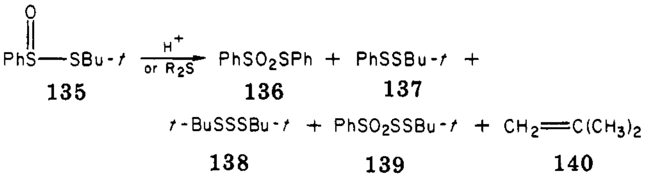


a, R = CH$_3$; b, R = (CH$_2$)$_4$

SCHEME XI

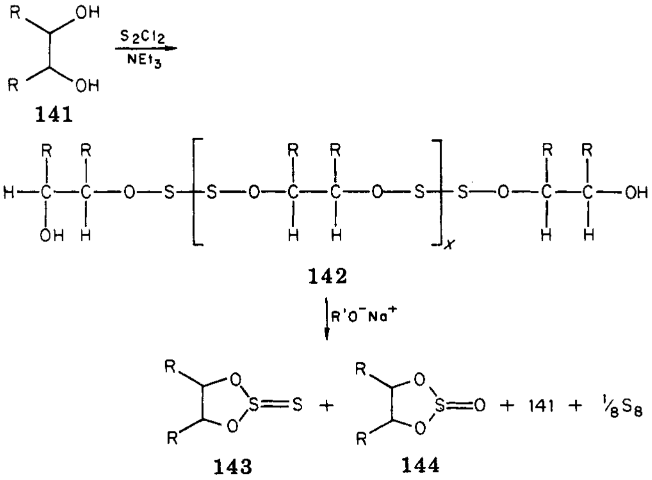


SCHEME XII



VI. Thionosulfites

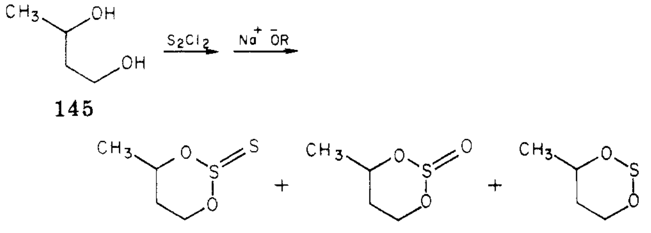
In 1950, at a time when no stable thiosulfoxides (R$_2$S=S) were known, Foss reasoned[2a,b] that sulfur-branched species involving d orbital expansion of the central sulfur atom could only be stable when this atom was attached to strongly electron-withdrawing groups (e.g., fluoro or alkoxy). This hypothesis was later confirmed experimentally both by Kuczkowski, in studies on sulfur monofluoride,[120] and by Thompson and his co-workers. The latter, in a series of papers,[121] reported the preparations of dialkoxy disulfides (**149**) and their branched-chain thionosulfite isomers (cf. **143**).



When 1,2-diols (cf. **141**) were reacted with disulfur dichloride, in the presence of triethylamine, polymeric products, with gross composition corresponding to 142, were obtained. These macromolecules could then be degraded by alkoxide catalysis to the appropriate thionosulfite **143**, sulfite **144**, and starting diol **141**. The crystalline thionosulfite products, unstable to prolonged exposure to light and room temperature, were characterized by combustion elemental analysis, molecular weight determination, and their spectral properties.[121]

Treatment of the 1,2-diols **141** with disulfur dichloride in the presence of triethylamine or methylmagnesium bromide, under conditions of high dilution, afforded products **143** and **144** directly.[121]

Extension of this work to 1,3-diols allowed[121c] the preparation (from 1,3-butanediol (**145**)) of thionosulfite **146**, along with the corresponding sulfite **147** and sulfoxylate **148**.



145

146 147 148

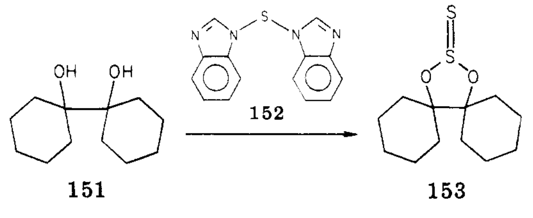
Support for the thionosulfite structures **143** was afforded[121] mainly by the similarity of their NMR spectra to those of the sulfites **144**.[121,122] The thionosulfites **143** absorbed around 250 nm (ε 2200–2600) in the ultraviolet, and this may be attributed to the >S=S linkage.

Thompson's studies[121] not only gave experimental proof for the existence of thionosulfites but also allowed assessment of the validity of the previous claimed preparations of this class of compounds. It seems clear from his work that the compounds prepared by Lengfeld[123] Meuwsen,[124] and others[125] are dialkoxy disulfides ROSSOR (**149**)[121b] and not the branched forms ROS(=S)OR (**150**). Previously evidence had been amassed both in favor of and against the branched structure **150**. Lengfeld[123] reacted sodium alkoxides with disulfur dichloride and obtained products that he presumed had the disulfide structure **149**. Meuwsen,[124] analyzing the results of a similar experiment, claimed to have obtained a mixture of both **149** and **150**, the latter being colored. This result was shown to be spurious[126] in that the coloration was merely caused by sulfur chloride impurities.

Physical data, in the form of parachor,[125a] and dipole moment[39] measurements were consistent with the dialkoxy disulfide formulation **149**. Raman spectral studies[37,127] lent further support to these results, in that the observed frequency of the S–S bond, in the diethyl ester prepared by Lengfeld[123] (**149**, R = Et), was 510 cm^{-1}, close to that expected for a S–S single bond. The rotational barrier about the S–S bond in **149** (R = Et) has been estimated,[121] via NMR variable temperature studies,[128] to be 8–9 kcal/mol. This result favors the unbranched structure **149** since normal S–S single bonds have similar values.[131]

An equilibrium between the two isomers (**149** and **150**) may explain the facile loss of sulfur observed on treatment of **149** with alkoxide ion[125b] and with Lewis acids.[130] However, Foss has pointed out[2a,b] that chemical methods cannot be trusted to distinguish between the two possibilities (**149** and **150**), and recent studies[131] on the chemical reactivity of dialkoxy disulfides do not substantiate such an equilibrium.

Since Thompson's pioneering studies,[121] only one other thionosulfite preparation has been reported.[132] Treatment of the pinacol **151** with the benzimidazole sulfur transfer reagent **152** gave the thionosulfite **153** in 50% yield.



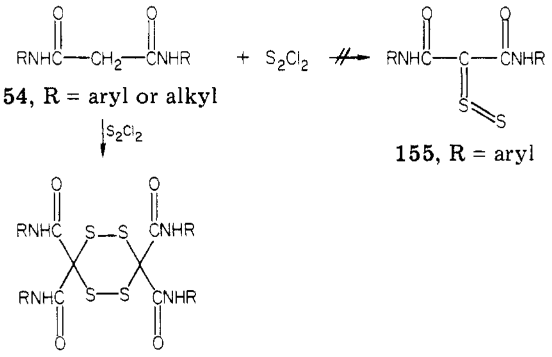
151 153

Elemental analysis, exact mass measurement, and the ^{13}C spectrum were consistent with structure **153**.[132] Recently the crystal structure was determined.[132b] The S–S bond length (1.901 Å) was clearly shorter than that for disulfides (2.02–2.06 Å)[133] and of the same order as those for F_2S_2 (1.86 Å),[134] S_2 (1.89 Å),[135] and the thiosulfinyl)amines—(-N=S=S) (see section VIII).

VII. Thiosulfines

This area has been reviewed very recently.[154b] The present section is included for the sake of completeness and to provide easy access to salient references and new data.

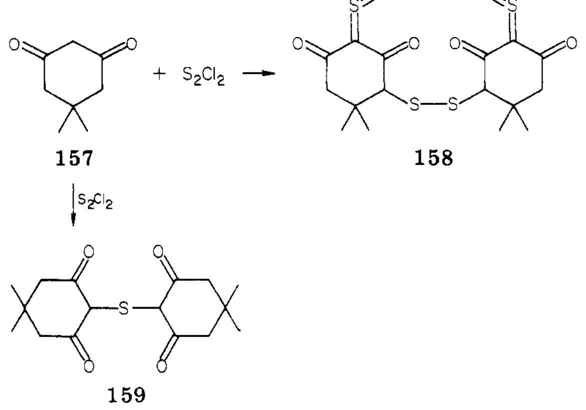
As yet not stable thiosulfines (>C=S=S) have been isolated, although several workers have proposed their transient existence. The putative stable thiosulfines **155** prepared by Naik,[17,136] from the reaction of disulfur dichloride with the malondiamides **154**, have been



154, R = aryl or alkyl

155, R = aryl

156, R = aryl or alkyl

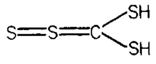


157 158

159

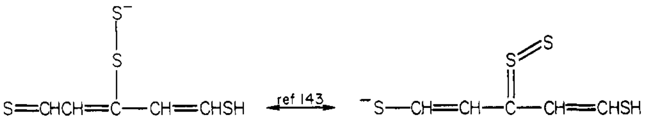
shown by one of us (G.W.K.) to have the dimeric structure **156**.[137] Similarly Naik's reported[17,136] preparation of the bis(thiosulfine) **158**, by the reaction of disulfur dichloride with 5,5-dimethyl-1,3-cyclohexanedione (**157**), is questionable in that a recent reinvestigation[138] of the reaction afforded only the sulfide **159**.[139]

A thiosulfine structure (**160**) has been assigned[140] to

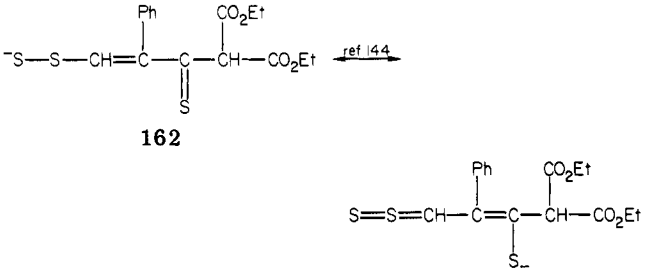


160

the product (H_2CS_4)[141] obtained by treatment of ammonium perthiocarbonate [$(NH_4)_2CS_4$] with formic acid.[142] However, in the absence of further physical and chemical studies, this structural assessment must remain tentative. Several authors[143-150] have reported dithioanion species (**161–168**) as intermediates. These may be equally well represented by the thiosulfine isomeric or resonance forms (**169–176**).

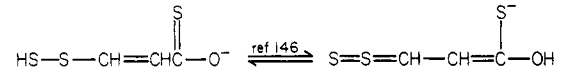


161 **169**

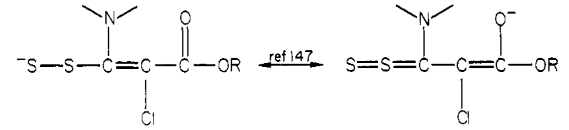


162 **170**

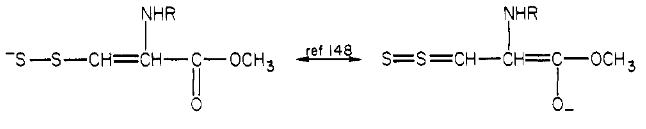
163 **171**



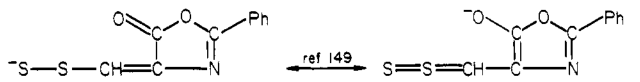
164 **172**



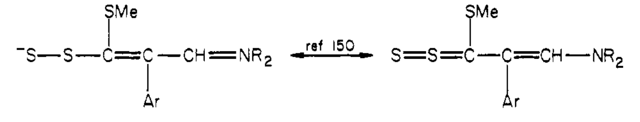
165 **173**



166 **174**

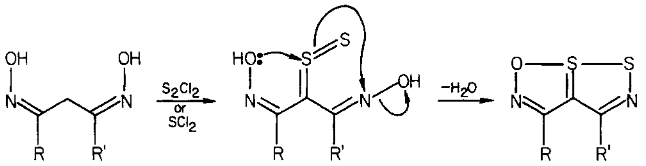


167 **175**



168 **176**

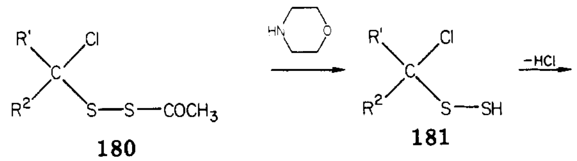
Thiosulfine intermediates **178** may also be involved in the formation of the dithiadiazapentalenes **179** from the reaction of disulfur dichloride (or sulfur dichloride) with the dioximes **177**.[151] Thiosulfine (**178**) intermediacy in the reaction of **177** with sulfur dichloride may



177 **178** **179**

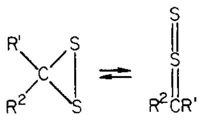
be rationalized in terms of initial thione formation and subsequent combination with SCl_2.[152]

Recently thiosulfines **183** have been proposed[154] as intermediates in the reaction of morpholine with the disulfides **180**. A likely pathway to **183** involves the



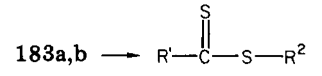
180 **181**

a, $R^1 = R^2 = Cl$;
b, $R^1 = C_6H_5S$;
$R^2 = 4\text{-}CH_3C_6H_4SO_2$;
c, $R^1 = R^2 = C_6H_5CO$



182 **183**

unstable (α-chloroalkyl)disulfanes **181** and hypothetical dithiiranes **182**. The intermediate **183a** could not be trapped with alkynes or strained alkenes but rearranged to the dithio ester **184a**, which on reaction with morpholine gave the stable compound **185**. Similarly the dithio ester **184b** reacted with morpholine to give the products **186** and **187**. In contrast, **180c** did not rearrange to a dithio ester; the intermediate thiosulfine **183c** was instead trapped directly by morpholine to form the disulfide **188**.



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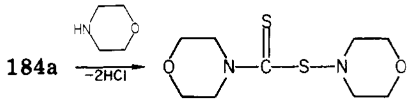

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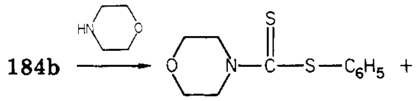

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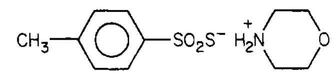

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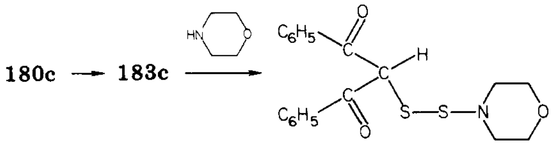
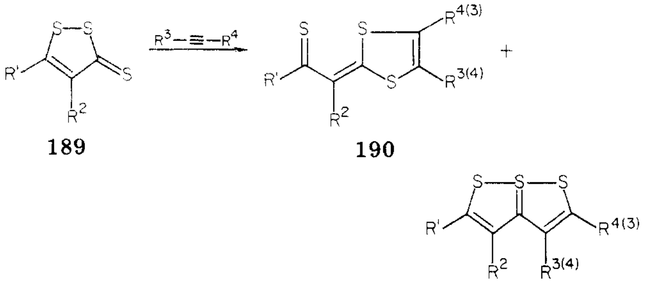


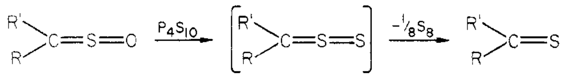
188

A thiosulfine has been postulated[154] as a precursor to the adducts **190** and **191** formed from reaction of alkynes with 1,2-dithiole-3-thiones **189**.[155]



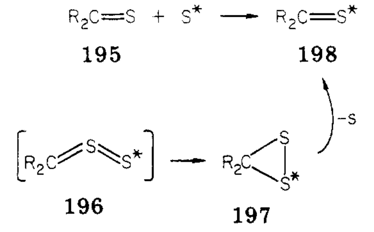
189 190 191

Very recent studies have indicated the presence of thiosulfine intermediates **193** in the reduction of sulfines



192 193 194

(cf. **192**) to thiones (**194**),[156] with P_4S_{10}. Thione formation, by loss of sulfur from a thiosulfine intermediate, has been previously postulated[196] (see section VIIIC7). Thiones **195** also react with radioactive sulfur to give the corresponding labeled thiones **198**, presumably via

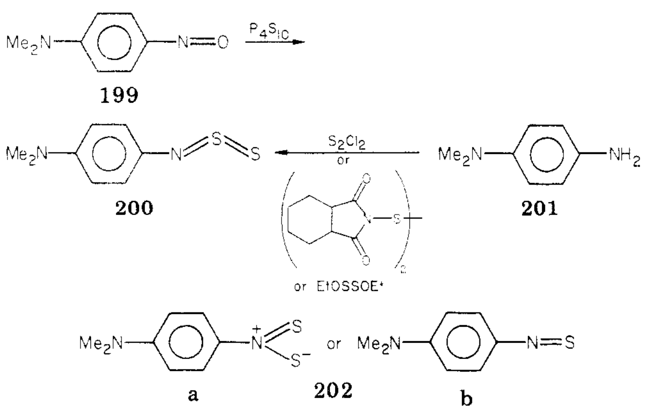


the thiosulfine (**196**) and dithiirane (**197**) intermediates.[157]

VIII. N-(Thiosulfinyl)amines

A. Preparation

The first stable *N*-(thiosulfinyl)amine) (**200**) was prepared by Barton and Robson, in 1974,[158] from the reaction of *N*,*N*-dimethyl-*p*-nitrosoaniline (**199**) with tetraphosphorus decasulfide. The structural assign-

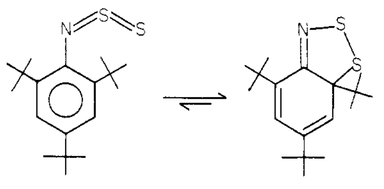


199 200 201 a 202 b

ment was verified both by unambiguous synthesis, from *N*,*N*-dimethyl-*p*-phenylenediamine (**201**) and disulfur dichloride, and from the nature of the cycloadducts obtained by reaction of **200** with dienes such as norbornadiene. Other possible structures (cf. **202**) were eliminated on the basis of these results. It seems likely that **200** is formed via the intermediate thionitroso compound **202b**.

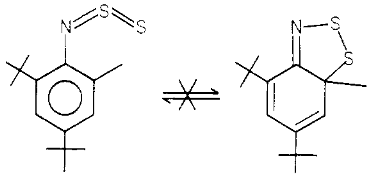
The structure of **200** was later verified by its preparation from **201** and diethoxy disulfide.[159]

Inamoto and co-workers demonstrated[160] that the sterically hindered *N*-(thiosulfinyl)-2,4,6-tri-*tert*-butylaniline (**203**) existed in equilibrium with the unique 5*H*-1,2,3-dithiazole **204**.



203 204

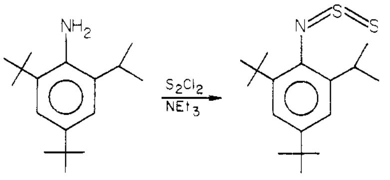
This equilibrium was not observed[160] for *N*-(thiosulfinyl)-2,4-di-*tert*-butyl-6-methylaniline (**205**), and



205

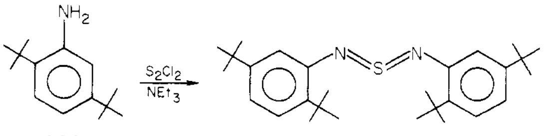
under similar reaction conditions as used for the preparation of **203**, 2,4,6-trimethylaniline and disulfur dichloride did not form an *N*-(thiosulfinyl) compound,[160,161] although the latter is apparently produced in low yield when the reaction and workup procedures are performed at lower temperatures.[160]

The isomerization (**203** $\rightleftharpoons$ **204**) was rationalized[160] as occurring via a cycloaddition of the $—N{=}S{=}S$ moiety with one of the relatively electron-rich C=C bonds[158] in the sterically hindered aryl system of **203**. It seems likely that plararity between the [(thiosulfinyl)amino] and aryl groups is precluded in **203** but less so in **205**. Thus, resonance stabilization of the $—N{=}S{=}S$ moiety in **205** may account for the difference in stabilities of **203** and **205**. 2,4-Di-*tert*-butyl-6-isopropylaniline (**206**) reacted with disulfur dichloride to give the corresponding *N*-(thiosulfinyl)aniline (**207**) as an unstable



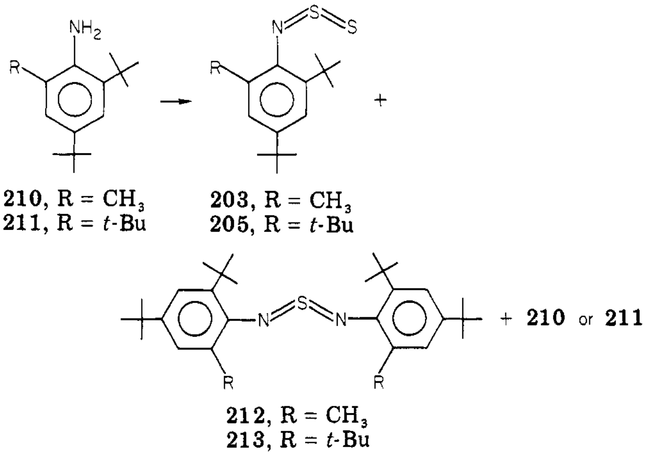
206 207

purple oil.[160b] The relative stability of the *N*-(thiosulfinyl)aniline **205**, compared to **207**, is noteworthy and has been rationalized[162b] (section VIIIC). A similar reaction with 2,5-di-*tert*-butylaniline (**208**) afforded[160b] only the sulfur diimide **209**, thus indicating the importance of bulky substituents at both ortho positions.



208 209

Surprisingly, treatment of the anilines **210** and **211** with sulfur dichloride (SCl_2) gave the *N*-(thiosulfinyl)anilines **203** and **205**, respectively.[160b] The sulfur diimides **212** or **213** and unreacted starting amines were also isolated. The formation of the *N*-(thiosulfinyl)anilines was ascribed to the known[163] partial dissociation of sulfur dichloride into disulfur dichloride and chlorine. However, in view of the presumably low concentrations of disulfur dichloride present in the mixture, it seems reasonable to assume that the (thiosulfinyl)amine product **203** or **205** can also arise from the reaction of a thionitroso (—N=S) intermediate[164] with sulfur dichloride. *N*-(Thiosulfinyl)amines (**216**) have also been prepared[165] by the treatment of *N*-*tert*-butyl-, *N*-(1-methyl-1-cyanoethyl)-, and *N*-(2,4,6-tribromophenyl)dichlorosulfimides (**214a–c**) with hexamethyldisilthiane (**215**). Only sulfur diimides (—N=S=N—) were obtained when other dichlorosulfimides, containing less electron donating or less sterically hindered groups attached to nitrogen, were reacted with **215**. No other stable alkyl-*N*-(thiosulfinyl)amines have been isolated[166] although the intermediacy of *N*-(thiosulfinyl)amines, in the preparation of alkylsulfur diimides **218** from *N*,*N*-bis(trimethylsilyl)amines (**217**) and disulfur dichloride, has been postulated.[167]



210, R = CH_3
211, R = *t*-Bu

203, R = CH_3
205, R = *t*-Bu

212, R = CH_3
213, R = *t*-Bu

$$\underset{\mathbf{214}}{\mathrm{RN{=}SCl_2}} + \underset{\mathbf{215}}{\mathrm{S(Si(CH_3)_3)_2}} \rightarrow \underset{\mathbf{216}}{\mathrm{RN{=}S{=}S}}$$

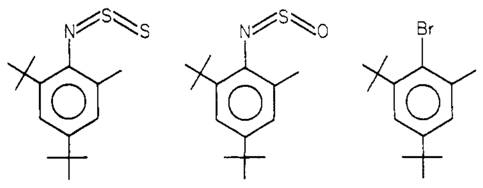
a, R = *t*-Bu; **b**, R = $(CH_3)_2C(CN)$;
c, R = 2,4,6-$Br_3C_6H_2$

$$\underset{\mathbf{217}}{\mathrm{R{-}N(SiMe_3)_2}} \xrightarrow{S_2Cl_2} [\mathrm{R{-}N{=}S{=}S}] \xrightarrow{RNSS} \underset{\mathbf{218}}{\mathrm{R{-}N{=}S{=}N{-}R}}$$

R = aryl or alkyl

B. Physical Properties

1. Dipole Moments

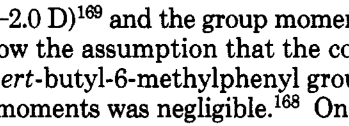


205, 1.51 D **219**, 2.05 D **220**, 1.63 D

Recently the dipole moment for 2-methyl-4,6-di-*tert*-butyl-*N*-(thiosulfinyl)aniline (**205**) was measured and compared[168] to the values obtained for the *N*-(sulfinyl) derivative (**219**) and 2,4-di-*tert*-butyl-6-methylbromobenzene (**220**). The measured dipole moments for **219** and **220** [2.05 and 1.63 D, respectively) were similar enough to values reported for *N*-sulfinylaniline (1.9–2.0 D)[169] and the group moment for Br (1.54 D)[170] to allow the assumption that the contribution of the 2,4-di-*tert*-butyl-6-methylphenyl group to the overall dipole moments was negligible.[168] On this basis the experimental dipole moment (1.51 D) for **205** was assumed to be due to the group moment of the (thiosulfinyl)amino group. The ratio of the negative charge on the sulfur(II) of the —N=S=S group to that on the nitrogen ($\delta S^-/\delta N^-$) was calculated to be 3.8 from the estimated bond moments for S=S and N=S bonds (2.60 and 0.55 D, respectively) and crystallographic data for the [(thiosulfinyl)amino] group of **205**.[171] The corresponding ratio ($\delta O^-/\delta N^-$) for the —N=S=O group was 8.7.

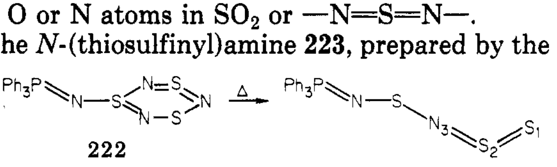
2. X-ray Crystallographic Measurements

X-ray crystallographic analysis has shown[171] that the *N*-(thiosulfinyl)amine **205** has a *Z* configuration in the crystalline state. The N–S and S–S bond lengths determined for **205** were 1.543 and 1.901 Å, respectively. Similar results were obtained for the unusual [(thiosulfinyl)amino]thio compound **221**, prepared by reaction of the N-unsubstituted piperidine with disulfur dichloride followed by treatment with aqueous ammonia.[172a] The measured bond lengths for the N_1–S_1 and S_1–S_2 bonds in **221** were 1.569 and 1.912 Å, respectively. These are significantly shorter than the reported N–S (1.60–1.76 Å)[173] and S–S (2.0–2.1 Å)[173] single bond lengths. The —N=S=S bond angle was determined[172a] to be 114.9° as compared to 120.4° and 117.0° for O=S=O[174] and —N=S=N—,[175] respectively. This smaller angle was attributed[172a] to a weaker repulsive force between N_1 and S_2 in **221** than those between the two O or N atoms in SO_2 or —N=S=N—.



221

The *N*-(thiosulfinyl)amine **223**, prepared by the action of heat on 222, gave analogous results.[172b] The measured[172b] bond lengths for the N_3–S_2 and S_2–S_1 bonds in **223** were 1.592 and 1.908 Å, respectively, and the —N=S=S bond angle was shown[172b] to be 111.4°.



222

223

3. Spectroscopic Measurements

a. Infrared Spectra. The infrared spectra of various *N*-(thiosulfinyl)anilines have been reported (Table V). No assignment of frequency values to particular vibrational modes in the molecules has been made.

TABLE V

compd	phase	IR spectrum, cm^{-1}	ref
200	nujol	1605, 1535, 1315, 1290, 1180, 830, 680	158
205	KBr	2950, 1590, 1455, 1360, 1222, 1169, 995, 870, 690, 650, 620	160
207	neat	1595, 1360, 1128, 1000	160b
216b	neat (film)	2990, 2950, 1570, 1460, 1390, 1205, 1160, 1090, 995, 795, 690	165

b. Ultraviolet Spectra. The normally weak absorption around 530 nm in the ultraviolet spectra of *N*-(thiosulfinyl)anilines (Table VI) has been attributed[160] to the (thiosulfinyl)amino moiety.

c. Nuclear Magnetic Resonance (NMR) Spectra. The factors influencing the equilibrium between **203** and **204** in solution were studied by using variable temperature nuclear magnetic resonance spectroscopy.[176] The interconversion between **203** and **204** was slow enough to show two distinct sets of NMR signals due to the two tautomers. Accordingly equilibrium constants were calculated on the basis of the NMR signal intensities for the two olefinic protons of **204** (δ 5.87 and 6.39, each d, J = 2Hz, 1 H) and the two aromatic protons of **203** [δ 7.34, s, 2 H).[176] In the temperature range 11–63 °C the predominant isomer was **204** but the relative amount of **203** increased substantially with increased temperature. From the calculated equilibrium constant (K = [204]/[203]), at different temperatures, $-\Delta G$ values (ranging from 1.68 to 1.09 kcal mol^{-1} at 11 °C to 63 °C, respectively) were obtained. These values permitted estimates for the heat of isomerization ($\Delta H = -4.9$ kcal mol^{-1}) and the entropy of isomerization ($\Delta S = -11.3$ cal mol^{-1} deg^{-1}) to be made.

The exothermicity of this unusual ring formation (**203** → **204**) was attributed[176] to both the decreased aromaticity caused by steric congestion and the considerable reactivity of the (thiosulfinyl)amino group toward a double bond (see section VIIIC7). No such ring formation, in the case of 2,4-di-*tert*-butyl-6-methyl-*N*-(thiosulfinyl)aniline (**205**), was observed by NMR spectroscopy over a temperature range of −102 to 70 °C. The variation of the equilibrium constant (K = [204]/[203]) with polarity of solvent (hexane to acetonitrile) was also investigated by NMR spectroscopy.[176] The increase in K with increasing polarity of solvent suggested that the dipole moment of **204** was larger than that for **203**, a result in agreement with the measured dipole moment for **204** (ca. 2.9 D)[177] and the estimated dipole moment for **203** [assumed similar to the value for **205** (1.51 D)[168]].

C. Chemical Properties of *N*-(Thiosulfinyl)anilines

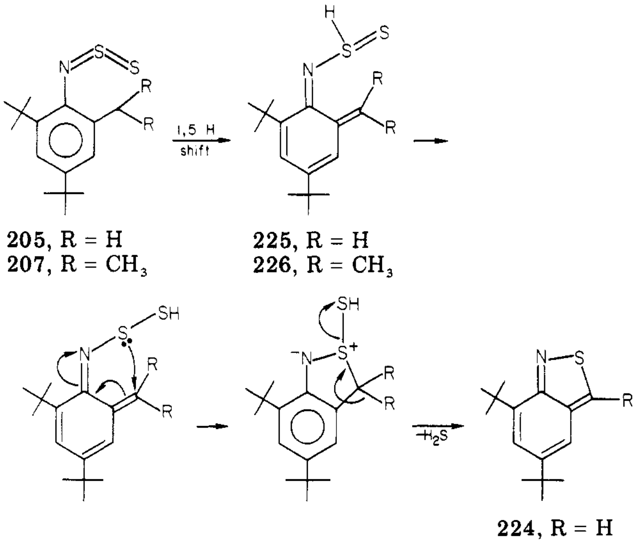
1. Thermolysis

Pyrolysis of 4-(dimethylamino)-*N*-(thiosulfinyl)aniline (**200**) at 200 °C gave sulfur and the corresponding azo compound,[158] whereas thermolysis of *N*-*tert*-butyl- and *N*-(2,4,6-tribromophenyl)-*N*-(thiosulfinyl)amines (**214a** and **214c**, respectively) afforded the corresponding sulfur diimides (—N=S=N—).[165] Sulfur diimides are known, however, to form azo compounds thermally.[167]

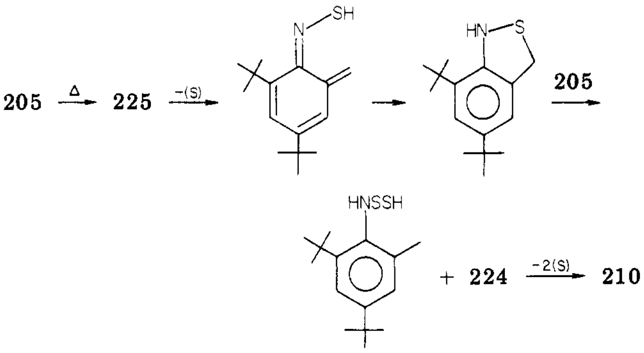
TABLE VI

compd	solvent	UV spectrum, nm, (ϵ)	ref
200	methanol	238 sh (4600), 262 sh (5900), 285 (7200), 350 (1700), 538 (39 000)	158
	cyclohexane	255 (7400), 284 (7100), 348 (3300), 510 (38 400)	158
203	hexane	240 sh (4720), 268 (2610), 292 (2580), 340 (2050), 410 (3480) 535 sh (v weak)	160
205	hexane	270 sh (1470), 310 sh (1940), 343 (5590), 476 (2190), 536 sh (1190)	160
207	pentane	272 sh (2060), 305 sh (2330), 343 (6960), 483 (1810), 542 sh (1130)	160

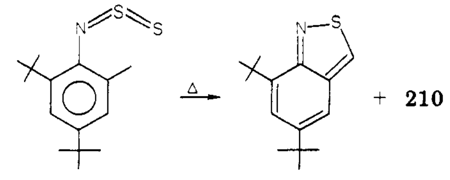
SCHEME XIII



SCHEME XIV



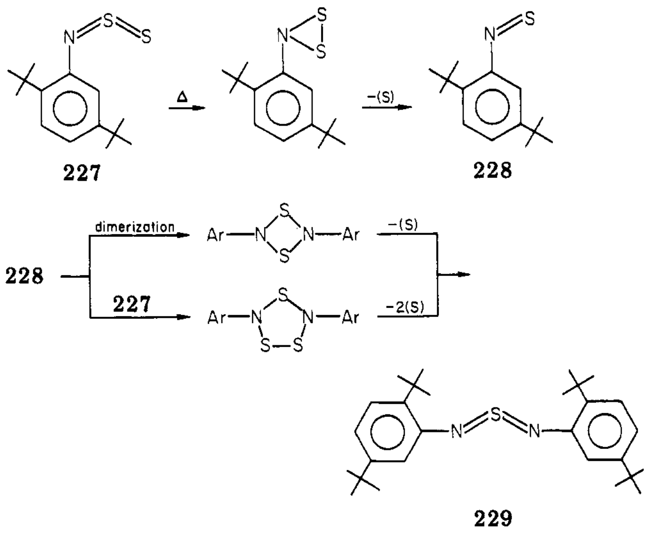
Thermolysis of **205** in benzene gave benzisothiazole **224**, the aniline **210**, and sulfur.[162]



205 224

The formation of **224** was rationalized in terms of an initial 1,5 hydrogen shift.[162] The subsequent mechanistic pathway is unclear, although two possible routes (Schemes XIII, XIV) have been suggested.[162] The former seems the most likely by analogy with the mechanism established for the thermal conversion of

SCHEME XV



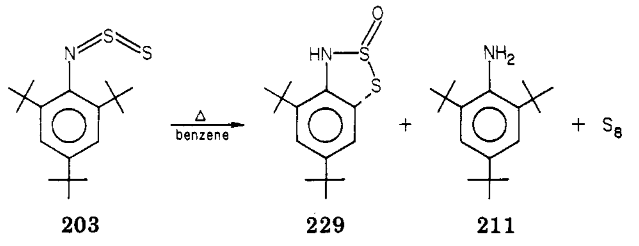
2,4-di-*tert*-butyl-6-methylnitrosobenzene to a benzisoxazole via an initial 1,5 hydrogen shift.[178,179] The relative stabilities of the *N*-(thiosulfinyl)anilines **205** and **207** (**205** > **207**) can thus be explained by the formation of a more stable intermediate (**226**) (cf. **225**) from 2,4-di-*tert*-butyl-6-isopropyl-*N*-(thiosulfinyl)aniline (**207**).[162b]

The formation of the sulfur diimide **209**, by treatment of 2,5-di-*tert*-butylaniline (**208**) with disulfur dichloride (see section VIIIA), was rationalized[162b] in terms of thermal decomposition of the initially formed, presumably unstable, *N*-(thiosulfinyl)aniline **227** to the reactive thionitroso compound **228** and subsequent dimerization, or reaction with excess **227**, followed by loss of one or more sulfur atoms (Scheme XV).

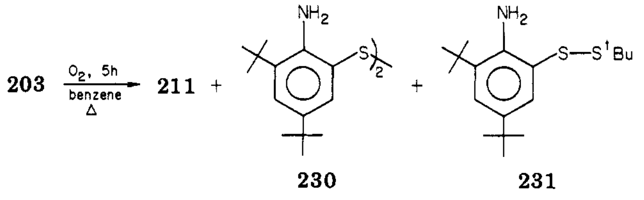
The thermolysis of **205**, yielding **224** and **210** may also be explained[162] in terms of initial decomposition to a thionitroso compound, conversion to a sulfur diimide intermediate **212**, and subsequent disproportionation of the latter, also via a 1,5 hydrogen shift (Scheme XVI).

However, mechanistic routes involving the intermediacy of a thionitroso compound cannot explain the fact that the 6-methyl derivative **205** is more stable than the 6-isopropyl derivative **207**.

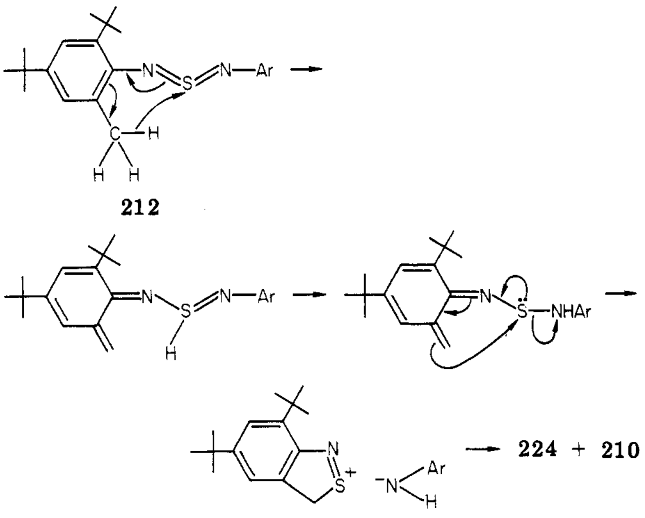
Unexpectedly, thermolysis of **203**, under nitrogen, gave the oxidized product **229** as well as the aniline **211** and sulfur.[162b]



Thermolysis of **203** under a stream of oxygen afforded a complex mixture of products from which **211**, **230**, and **231** were isolated.

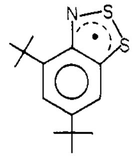


SCHEME XVI



Ar = 2,4-(t-Bu)$_2$-6-MeC$_6$H$_2$-

An ESR signal (a_N = 82 G, g = 2.008) was obtained on thermolysis of **203** for 5 min at 110 °C in degassed benzene. This peak was ascribed[162b] to a nitrogen-centered radical **232** by analogy with results obtained



232

for other sulfur-containing nitrogen-centered radicals.[180–182]

A pathway leading to the formation of **229** has been proposed,[162b] but with the present experimental data the mechanism remains unclear.

2. Photolysis

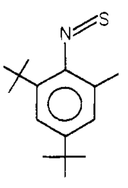
Irradiation of **205** through pyrex, with light from a

$$\mathbf{205} \xrightarrow{h\nu} \underset{\mathbf{210}}{\mathrm{ArNH_2}} + \underset{\mathbf{212}}{\mathrm{Ar{-}N{=}S{=}N{-}Ar}} + \mathrm{S_8}$$

$$\mathrm{Ar} = 2,4\text{-}(t\text{-Bu})_2\text{-}6\text{-MeC}_6\mathrm{H}_2\text{-}$$

medium-pressure mercury lamp afforded the aniline **210**, sulfur diimide **212**, and sulfur in various yields, depending on concentration, solvent, and irradiation time.[162]

The progress of the reaction could be followed by observation of the changes in the electronic spectrum on irradiation of **205** in an EPA matrix at 77 K. A large increase in absorption at 473 nm (ε ~ 15000) was detected, and this was postulated[162b] as arising via the presence of one of three species (**233**–**235**). A nitrenoid intermediate was eliminated on the basis of the known absorption characteristics (≥400 nm, ε a few hundred) of such a species.[183] Similarly sulfur atom or its oli-



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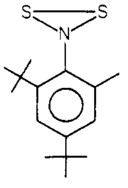

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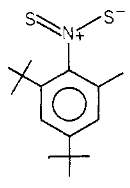


235

gomers could not be responsible for the 473-nm peak since their absorptions are below 420 nm.[184]

The aniline **210** may arise from photodecomposition of the sulfur diimide **212** since irradiation of **212** gave only **210** and unchanged **212**.[162]

When the equilibrium mixture of **203** and **204** was

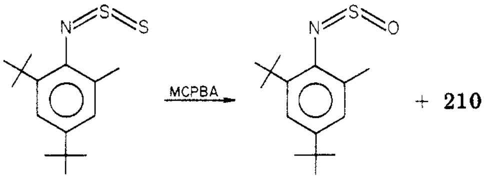
$$\mathbf{203} \rightleftharpoons \mathbf{204} \xrightarrow{h\nu} \underset{\mathbf{211}}{\mathrm{ArNH_2}} + \underset{\mathbf{213}}{\mathrm{Ar{-}N{=}S{=}N{-}Ar}}$$

$$\mathrm{Ar} = 2,4,6\text{-}(t\text{-Bu})_3C_6H_2\text{-}$$

irradiated in pentane a complex mixture arose, from which the aniline **211** and the sulfur diimide **213** were isolated.[162]

3. Oxidation

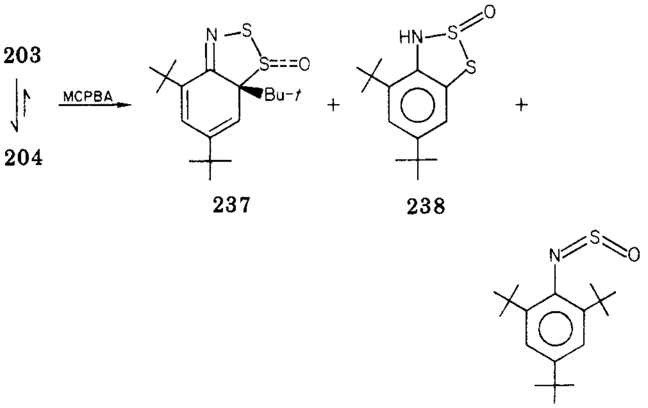
Reaction of the (thiosulfinyl)aniline **205** with *m*-chloroperoxybenzoic acid (MCPBA) (1 equiv.) gave the sulfinylaniline **236**, the aniline **210**, and unreacted starting material.[185]



205 236

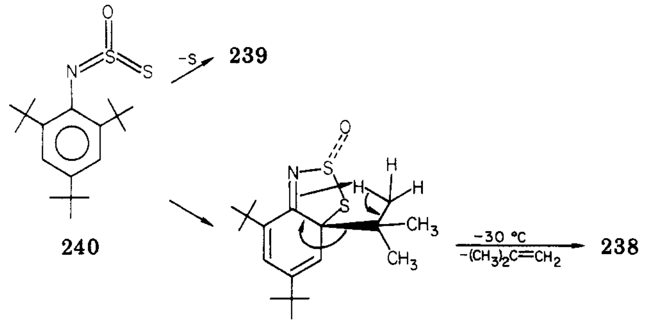
The aniline **210** is known to react with MCPBA to form 2,4-di-*tert*-butyl-6-methylnitrosobenzene,[186] and since this product was not isolated from the reaction mixture it was concluded[185] that the amine **210** was formed on workup.

Treatment of the equilibrium mixture (**203**, **204**) with MCPBA in dichloromethane afforded three isolable products (**237**–**239**),[185,187] which were characterized by spectroscopic, chemical, and, in one case,[188] X-ray crystallographic analyses.



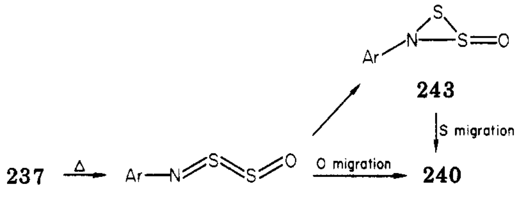
237 238 239

Thermal decomposition of **237** gave both **238** and **239** as well as 2,4,6-tri-*tert*-butylaniline. This unusual transformation to **238** and **239** was, apparently,[185,187] the first direct observation of oxygen transfer in thiolsulfinate type compounds.[189,190] The formation of products **238** and **239** was rationalized[185,187] in terms of a single intermediate **240** from which sulfur extrusion would afford **239**, and, more interestingly, an initial cyclization to 241 followed by a retro-ene type transformation could yield **238**.



240 241

Although the bicyclic compound **241** could not be isolated, distinct spectral evidence for its intermediacy was obtained.[185,187] The formation of **241** was rationalized[185] in terms of two possible mechanistic pathways: via oxygen migration from **242** or sulfur migration from **243**. Available experimental evidence does not allow for distinction between these two possibilities.



242

Ar = 2,4,6-*t*-Bu₃C₆H₂-

4. Reduction

Barton and Robson[158] have briefly examined the reduction of the (thiosulfinyl)amino group by treatment of *p*-(dimethylamino)-*N*-(thiosulfinyl)aniline (**200**) with sodium borohydride and hydrogen sulfide. The product of reduction, viz. *N*,*N*-dimethyl-*p*-phenylenediamine (also obtained by acid hydrolysis) was identified as its benzoyl derivative, *N'*-benzoyl-*N*,*N*-dimethyl-*p*-phenylenediamine.

A trace of hydrogen sulfide was detected (as PbS) during the thermolysis of 2,4-di-*tert*-butyl-6-methyl-*N*-(thiosulfinyl)aniline (**205**)[162] [see section VIIIC], and it was proposed[162] that the aniline product **210** was thus formed by H_2S reduction of **205**. The likelihood of such a reaction was confirmed in a separate experiment.

5. Reaction with Electrophiles

The *N*-(thiosulfinyl)amines **216** [see section VIIIA]

$$\mathbf{216a{-}c} \xrightarrow{2Cl_2} \underset{\mathbf{244}}{\mathrm{RN{=}SCl_2}} + SCl_2$$

a, R = *t*-Bu; **b**, R = $(CH_3)_2C(CN)$; **c**, R = 2,4,6-$Br_3C_6H_2$

reacted rapidly with chlorine gas at room temperature, to form the appropriate N-substituted dichlorosulfimides **244**.[165]

A ready reaction of compounds **216** with bromine was

$$\mathbf{216a} \xrightarrow{Br_2} \underset{\mathbf{245}}{\mathrm{(CH_3)_3CN{=}SBr_2}} + S_2Br_2$$

also observed,[165] but only *N*-*tert*-butyl-*S*,*S*-dibromosulfimide (**245**)[191] could be isolated in pure form.

Contrastingly, when the *N*-(thiosulfinyl)aniline **205** was

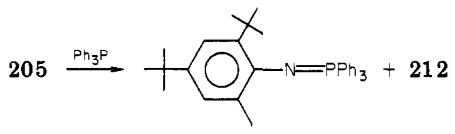
$$\underset{\mathbf{205}}{\mathrm{ArN{=}S{=}S}} \xrightarrow{\mathrm{Br_2}} \underset{\mathbf{212}}{\mathrm{ArN{=}S{=}NAr}} + \mathrm{S_8}$$

$$\mathrm{Ar} = 2,4\text{-}t\text{-}\mathrm{Bu_2}\text{-}6\text{-}\mathrm{MeC_6H_2}$$

treated with an equimolar amount of bromine, at room temperature, the products were the sulfur diimide **212** and elemental sulfur,[185] possibly via an intermediate thionitroso compound **233**.[185] Other electrophilic reagents such as trimethylsilyl chloride and trimethyloxonium tetrafluoroborate did not react with **205** at room temperature.[185]

6. Reaction with Nucleophiles

a. With Phosphines and Phosphites. Treatment of **205** with triphenylphosphine gave,[192] even at −78 °C, the sulfur diimide **212** and the iminophosphorane **246**



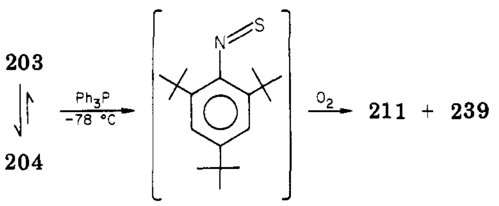
246

in 21% and 66% yield, respectively.[193] The reaction of the equilibrium mixture (**203**, **204**) with triphenyl-phosphine, under similar conditions, afforded[192] no iminophosphorane product but instead the aniline (**211**), sulfur diimide (**213**), and sulfinylaniline (**239**) derivatives in 38.6%, 34.4%, and 11.0% yield, respectively.[193]

$$\mathbf{203} \rightleftharpoons \mathbf{204} \xrightarrow{\mathrm{Ph_3P}} \underset{\mathbf{211}}{\mathrm{ArNH_2}} + \underset{\mathbf{213}}{\mathrm{ArN{=}S{=}NAr}} + \underset{\mathbf{239}}{\mathrm{ArN{=}S{=}O}}$$

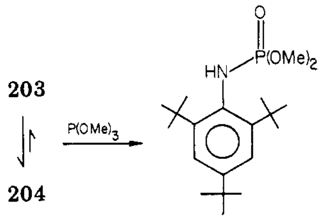
$$\mathrm{Ar} = 2,4,6\text{-}t\text{-}\mathrm{Bu_3C_6H_2}$$

Repetition of the previous experiment, under a stream of oxygen, gave only **211** and **239** in 35.4% and 38.6% yield, respectively. The absence of the sulfur diimide **213** in the product mixture led to the conclusion[192] that **211** and **239** were produced from the unstable (thionitroso)benzene (**247**) intermediate, which could be trapped.



247

A nitrenoid intermediate was excluded[192] by the absence, from the reaction mixture, of products expected for such a species by analogy with the known[194] nitrene producing reaction of the corresponding nitroso compounds with trialkylphosphines.



248

The phosphoramidate **248** was formed slowly upon reaction of the equilibrium mixture **203**, **204** with excess trimethyl phosphite.[192]

b. With Organometallic Reagents. Treatment of the *N*-(thiosulfinyl)amine **205** with an equimolar

$$\underset{\mathbf{205}}{\mathrm{Ar{-}N{=}S{=}S}} \xrightarrow[n\text{-BuLi}]{\mathrm{CH_3MgI\ or}} \underset{\mathbf{210}}{\mathrm{ArNH_2}} + \underset{\mathbf{212}}{\mathrm{Ar{-}N{=}S{=}N{-}Ar}}$$

$$\mathrm{Ar} = 2,4\text{-}t\text{-}\mathrm{Bu_2}\text{-}6\text{-}\mathrm{MeC_6H_2}$$

amount of methylmagnesium iodide or butyllithium gave the aniline **210** and the sulfur diimide **212**.[192] With excess isopropylmagnesium bromide only the aniline **210** was isolated.

One of us (K.T.)[195] has recently investigated the reaction of **205** with excess phenylmagnesium bromide,

$$\mathbf{205} \xrightarrow{\mathrm{PhMgBr}} \mathbf{210} + \mathbf{212} + \underset{\mathbf{249}}{\mathrm{PhSSPh}}$$

confirming the formation of the aniline **210** and sulfur diimide **212**. The disulfide **249** (presumably from reaction of excess Grignard with sulfur) and other, as yet unidentified, minor products were also formed.

c. With an Enamine. The aniline **210** was obtained by treatment of **205** with 1-(1-pyrrolidinyl)cyclopentene.[192] The expected 1:1 cycloadduct (see section VIIIC7) could not be detected, even at −78 °C.

$$\mathbf{205} \xrightarrow{\text{1-(1-pyrrolidinyl)cyclopentene}} \mathbf{210}\ (57.7\%)$$

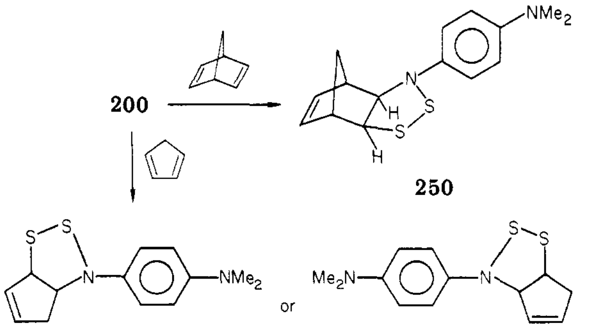
d. With Amines. The aniline **210** was also the sole isolable product from the reaction of **205** with various primary and secondary alkyl amines.[192] Even after 1 week, no reaction was observed between aniline (the only aromatic amine utilized) and **205**.

$$\mathbf{205} \xrightarrow[\text{or pyrrolidine}]{\mathrm{RNH_2}} \mathbf{210}$$

$$\mathrm{R} = n\text{-Bu},\ t\text{-Bu},\ \text{1-adamantyl}$$

7. Cycloaddition Reactions

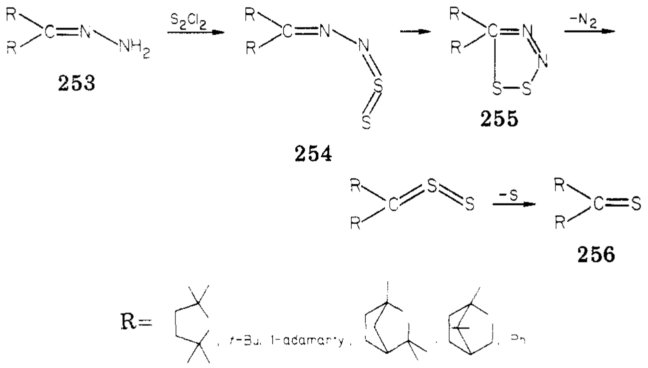
(Thiosulfinyl)amine **200** reacted with both norbornadiene and cyclopentadiene to give crystalline 1:1 adducts assigned the structures **250** and **251** or **252**, respectively.[158]



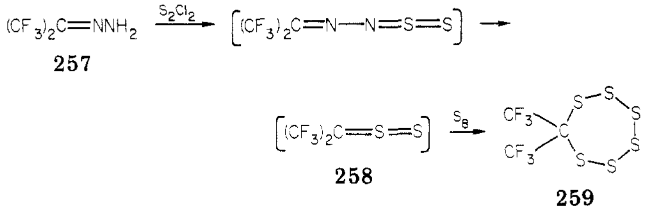
250

251 **252**

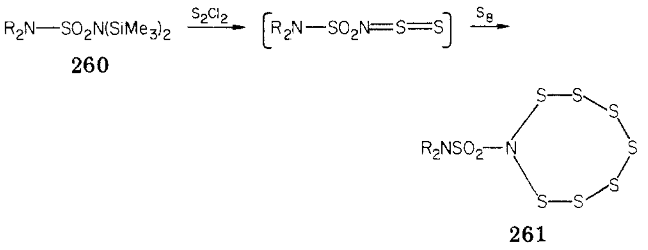
More recently an intramolecular cycloaddition of an intermediate (thiosulfinyl)amine **254** to a C=N bond was proposed[196] to explain the formation of a thione **256** from the reaction of a hydrazone **253** with disulfur dichloride.



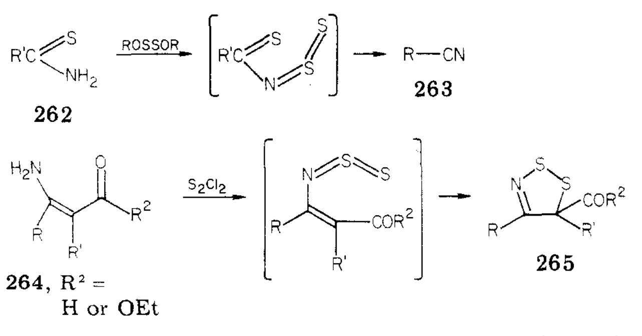
Interestingly, when hexafluoroacetone hydrazone (**257**) was treated with disulfur dichloride at −23 °C a low yield of the hexathiacycloheptane derivative **259** was obtained,[196b] presumably via reaction of an intermediate thiosulfine **258** with sulfur.



Similarly, treatment of *N*,*N*-bis(trimethylsilyl)-sulfonamides **260** with disulfur dichloride has been shown[197] to yield the eight-membered cyclic systems (**261**).



The intramolecular cyclization of the —N=S=S group to a multiple bond (cf. **254** → **255**) may well be a general phenomenon since such a reaction has been postulated to explain the formation of nitriles **263** from the reaction of thioamides **262** with dialkoxy disulfides (ROSSOR)[159] and the formation of 5*H*-1,2,3-dithiazoles **265** from β-keto enamines **264** and S_2Cl_2.



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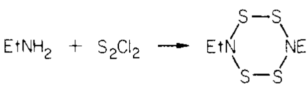
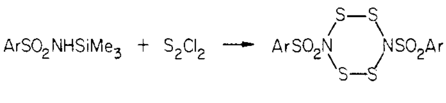
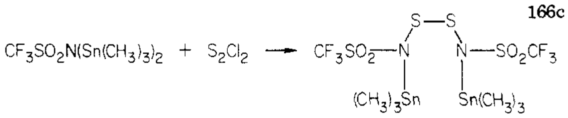

166a


166b

Also: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