

The Chemistry of Organic Polysulfanes R–S_n–R (*n* > 2)

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I. Introduction

Sulfanes and polysulfanes are covalent compounds of the type X–S_n–X, with *n* = 1, 2, ... and X being a

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Ralf Steudel was born in Dresden and received his degrees from the Freie Universität Berlin (Dipl.-Chem., 1963) and the Technische Universität Berlin (Dr.rer.nat., 1965). After his Habilitation in 1969, he became Professor of Inorganic Chemistry at the Technische Universität Berlin, where he has remained ever since, turning down chairs offered to him at the universities of Stuttgart and Cologne. He spent one year as a visiting professor at M. I. T. (Cambridge, MA) in 1973/74, where he worked with Professors Richard C. Lord and David F. Eggers at the Spectroscopy Laboratory. Ralf Steudel's research area is the chemistry of the nonmetals, in particular, sulfur and selenium chemistry. He has synthesized and structurally characterized 10 novel sulfur allotropes and seven new sulfur oxides as well as numerous other sulfur-rich and selenium-rich compounds, both inorganic and organic. More than 250 research papers on the synthesis, structures, spectra, and reactions of these compounds have originated from this work, which earned him more than 160 invitations to seminars and conferences worldwide. He is also known from his textbook *Chemie der Nichtmetalle*, which was translated into several foreign languages, as well as from his translations of foreign textbooks into German, for example, of the famous *Inorganic Chemistry – Principles of Structure and Reactivity* by James Huheey, Ellen Keiter, and Richard Keiter. In 1991 Ralf Steudel organized and chaired the 6th International Symposium on Inorganic Ring Systems in Berlin, from which the monograph "The Chemistry of Inorganic Ring Systems" (Elsevier: Amsterdam, 1992) originated. The Karl-Winnacker stipend was awarded to him for the period 1974–1979.

univalent group like hydrogen (sulfanes), halogen (halosulfanes), or an organic radical R (organosulfanes). For example, H_2S_3 is termed trisulfane, and S_4Cl_2 is dichlorotetrasulfane. Numerous compounds of these types are known since sulfur atoms have a high tendency to form homoatomic chains and rings as a result of the high S–S bond energy of 265 kJ mol⁻¹.^{1,2} Table 1 gives an overview of which chain lengths and ring sizes have so far been observed for the various polysulfane derivatives.

The organic polysulfanes described in this review are compounds of the type R–S_n–R with $n > 2$; they may be chain-like or cyclic. The organic residues (alkyl or aryl) are linked to the sulfur chain via carbon atoms. In the literature these compounds are

often termed as organic polysulfides, but the IUPAC recommended nomenclature is polysulfanes. The name polysulfide should only be applied to ionic compounds such as Na_2S_4 .

Sulfur-rich organic polysulfanes are somehow intermediates between organic and inorganic compounds. On one hand, they are characterized by organic substituents R which terminate the sulfur chain or close this chain to form a ring. On the other hand, compounds with sulfur chains of three or more sulfur atoms are "inorganic" enough to attract the interest of inorganic chemists who have contributed much to this area. Organic polysulfanes with up to 16 sulfur atoms in the molecule have so far been obtained as pure substances, but species with up to 35 sulfur atoms in a chain or ring have been prepared in mixtures. The correct nomenclature for compounds of the type R–S_n–R is diorganypolysulfane, but in this review the more convenient term organic polysulfane will mainly be used. Organypolysulfanes of the type RS_nH are also known; if $n = 2$, they are sometimes termed as hydropersulfides or hydrodisulfides. Organylchlorosulfanes RS_nCl are homologues of the sulfenyl chlorides RSCl and will be summarized under the latter name for the sake or brevity. If $n = 2$, they are sometimes termed thio-sulfenyl chlorides or chlorodisulfides in the chemical literature. The IUPAC nomenclature is, however, always based on the name sulfane even for derivatives such as R_2S and RSCl .

Organometallic polysulfanes such as 1,2,3-trithia-[3]ferrocenophane are not a topic of this review; their chemistry has recently been reviewed.³

Organic polysulfanes play an important role not only in basic research and in industry; they are also found as natural products in organisms and occur in the inanimate nature. In the latter case, they are partly of biotic, partly of abiotic (geochemical) origin and are widespread in sulfur-rich fossil fuel. Some of the polysulfanes produced by algae, mushrooms, or ascidians show biological activity which makes them interesting for the pharmaceutical industry (see Section VI). The main importance of organic polysulfanes comes, however, from their role in the large-scale industrial vulcanization of natural and synthetic rubber with elemental sulfur which in the early stages of the reaction results in sulfur-rich polysulfanes as will be described in Section VII.

The chemistry of organic polysulfanes is closely related to that of their oxidized derivatives. Therefore, in Table 2, the well-characterized sulfane oxide species with up to four sulfur atoms in the chain are

Table 1. Presently Known Sulfur Rings and Chains (n Represents the Chain Length or Ring Size)

type of compound	formula	n in pure compounds	n from spectroscopic or other evidence
sulfur homocycles	S_n	6–20	n up to 80
sulfanes (polysulfanes)	$\text{H}-\text{S}_n-\text{H}$	1–8	35
dichloropolysulfanes	$\text{Cl}-\text{S}_n-\text{Cl}$	1–7	30
diorganopolysulfanes	$\text{R}-\text{S}_n-\text{R}$	1–11	35
polysulfides	S_n^{2-}	1–8	
organopolysulfides	$\text{R}-\text{S}_n^-$	1	2
polythionates	$^- \text{O}_3\text{S}-\text{S}_n-\text{SO}_3^-$	1–4	22
sulfanemonosulfonates	$^- \text{S}_n-\text{O}_3^-$	1	2–13
bunte salts	$\text{R}-\text{S}_n-\text{SO}_3^-$	1	2

Table 2. Recommended Nomenclature of Organopolysulfanes and Their Oxidized Derivatives

sulfide (monosulfane)	R-S-R
sulfoxide (monosulfane oxide)	R-S(O)-R
sulfenate (sulfenic acid ester)	R-S-O-R
sulfinate (sulfinic acid ester)	R-S(O)-O-R
sulfonate (sulfonic acid ester)	R-S(O) ₂ -O-R
disulfane (disulfide)	R-S-S-R
disulfane monoxide (thiosulfinate)	R-S(O)-S-R
disulfane 1,1-dioxide (thiosulfonate)	R-S(O) ₂ -S-R
disulfane 1,2-dioxide (α-disulfoxide)	R-S(O)-(O)-R
Bunte salt (thiosulfate)	R-S-SO ₃ ⁻
disulfane monosulfonate	R-S-S-SO ₃ ⁻
trisulfane	R-S-S-S-R
trisulfane 1-oxide	R-S(O)-S-S-R
trisulfane 1,1-dioxide	R-S(O) ₂ -S-S-R
trisulfane 2-oxide	R-S-S(O)-S-R
trisulfane 1,3-dioxide	R-S(O)-S-S(O)-R
trisulfane 1,1,3,3,-tetroxide	R-S(O) ₂ -S-S(O) ₂ -R
tetrasulfane	R-S-S-S-S-R
tetrasulfane 1-oxide	R-S(O)-S-S-S-R
tetrasulfane 1,4-dioxide	R-S(O)-S-S-S(O)-R
tetrasulfane 2,3-dioxide	R-S-S(O)-S(O)-S-R
tetrasulfane 1,1,4,4,-tetroxide	R-S(O) ₂ -S-S-S(O) ₂ -R

presented. The systematic nomenclature based on the name sulfane is also given in Table 2. In addition, conventional names for some of these compounds are shown in parentheses.

In this article the preparation, structure, modern analysis, basic reactions, natural occurrence, biological activity, and practical importance of organic polysulfanes with three or more neighboring sulfur atoms in a chain or ring are reviewed. Previous reviews also included disulfanes (R₂S₂), and the emphasis was usually on the latter. The preparation of R₂S_n (n > 2) was reviewed by Schöberl and Wagner⁴ in 1955, by Wilson and Buchanan⁵ in 1976, by Field⁶ in 1977, by Gundermann and Hümke⁷ in 1985, and by Steudel and Kustos⁸ in 1994. Laur⁹ summarized the stereochemistry of (mainly) organic sulfur compounds in 1972. The analytical chemistry or organic polysulfanes was reviewed by Cardone¹⁰ in 1972. Reid¹¹ published a list of 76 organic polysulfanes (n > 2) known in 1960. A brief account on inorganic and organic polysulfanes by Pickering and Tobolsky¹² appeared in 1972. Since those days, however, considerable progress has been made. For trisulfanes and their oxides, this progress has been reviewed by Clennan and Stensaas in 1998.³

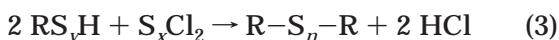
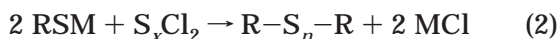
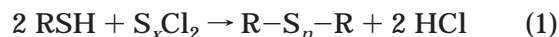
II. Synthesis

There are numerous reactions to prepare organic polysulfanes, which will be grouped in different sections according to the reagents used. Although there is normally no principal difference between the preparation of chain-like and cyclic polysulfanes R₂S_n, for convenience the two types will be treated separately. Which method to choose for the synthesis of a particular compound will depend on the available reagents, on the chemical reactivity of the organic group R, on the chances to separate the reaction mixture to produce pure substances, and on the amount of material needed. The following order of synthetic procedures is relatively arbitrary and should not be taken as a measure of relative importance or general applicability.

A. Chain-Like Polysulfanes

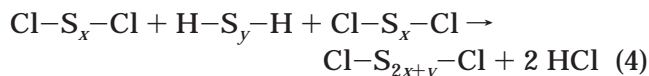
1. Reaction of Thiols, Thiolates, or Organysulfanes with Dichlorosulfanes

Alkyl- and arylpolysulfanes may be prepared by the classical reactions shown in eqs 1–3, with M = metal:^{4,5,7}

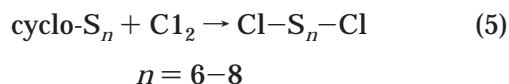


However, since only SCl₂ and S₂Cl₂ are commercially available, reactions 1 and 2 are primarily used to make tri- and tetrasulfanes. Reactions 1 and 3 are usually carried out in dry ether (or THF) or in a nonpolar solvent in the presence of an equivalent amount of a tertiary amine like pyridine to bind the sideproduct HCl.^{13–15} In the case of reaction 2, lead thiolates have also been found to be very useful.^{5,7} Unsymmetrical substitution is achieved by a stepwise reaction: first, 1 equiv of the thiol RSH is allowed to react with the sulfur chloride followed by addition of a different thiol R'SH.¹⁶

The more sulfur-rich dichlorosulfanes S_xCl₂ (x = 3–5) needed to make long-chain polysulfanes may be synthesized in analogous reactions from H₂S, H₂S₂, or H₂S₃ on one hand and an excess of SCl₂ or S₂Cl₂ on the other hand:¹⁷



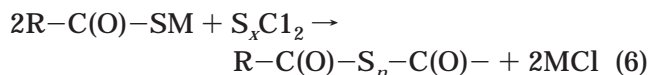
The longer-chain chlorosulfanes S_xCl₂ with x = 6–8 are best prepared by a carefully controlled ring-opening chlorination of the corresponding cyclo-S_n molecules (n = 6–8) with Cl₂ in CCl₄ at 0 °C:^{18–20}

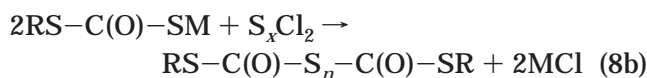
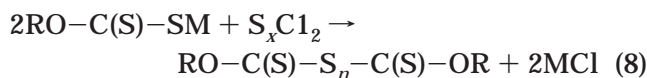
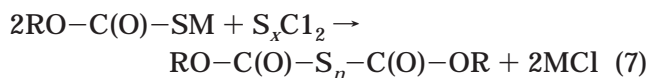


Examples. Substituted diphenyltrisulfanes (4-R'C₆H₄)₂S₃ with R' = NO₂, MeCO, EtOCO, MeS, MeO, and even NH₂ have been prepared by reaction 1. Since amino groups would also be attacked by SCl₂, this reaction was carried out in anhydrous acetic acid, resulting in the protonation of the -NH₂ group to -NH₃⁺, which is less reactive toward SCl₂.¹⁵ The bis-acetate obtained is converted to bis(4-aminophenyl)-trisulfane by reaction with sodium hydroxide.¹⁵

Dithiols react with dichlorosulfanes to cyclic organopolysulfanes; see Section II.B.2.

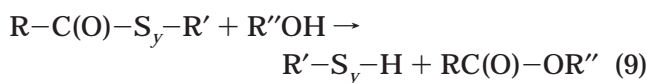
Reaction 2 has also been used to synthesize polysulfanes of thiocarbonic acids,²¹ alkoxythiocarbonic acids,^{22,23} (alkylthio)thiocarbonic acids,²² or alkoxydithiocarbonic acids (xanthates^{24–26}) (eqs 6–8, with M = H, Na, K and n = x + 2):





It should be noted that the polysulfanes obtained by reactions 8a and 8b are isomers.

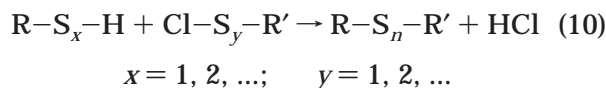
The organylpolysulfanes RS_yH needed for reaction 3 may be prepared from organylacylpolysulfanes by alcoholysis (eq 9 with $n = 2$ or 3):²⁷



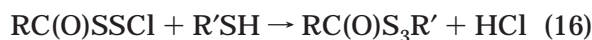
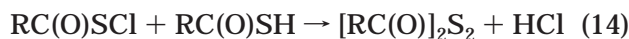
2. Reaction of Thiols or Organylpolysulfanes with Sulfenyl Chlorides

The condensation of thiols or organylsulfanes with sulfenyl chlorides, usually carried out in dry ether at 20 °C, allows the synthesis of symmetrically or unsymmetrically substituted polysulfanes. R and R' may be alkyl, aryl, or acyl groups;^{5,7} yields can be as high as 90%.

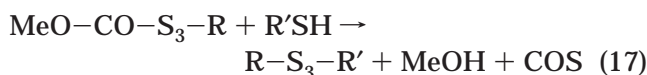
CF_3SSH without any solvent reacts at 20 °C with CF_3SCl to give the highly toxic $(\text{CF}_3)_2\text{S}_3$ and with CF_3SSCl to afford $(\text{CF}_3)_2\text{S}_4$.²⁸ The trisulfane can also be made from CF_3SCu and SCL_2 .^{28c} Unsymmetrical trisulfanes with various alkyl and aryl substituents²⁹⁻³¹ have been synthesized by reaction 10; bis(sulfenyl chlorides) $\text{R}(\text{SCl})_2$ react similarly:³²



The sulfenyl chlorides⁵ and their homologues needed for reaction 10 may be prepared by the reactions shown in eqs 11–13. For the synthesis of alkoxy carbonyl compounds,³³ reactions according to eqs 14–16 may be applied:



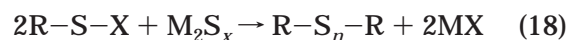
Since the latter polysulfanes react with thiols in the presence of a base according to eq 17, they have been used to synthesize various unsymmetrical trisulfanes in good to excellent yields (25–100%):³⁴



Because of the mild reaction conditions (–78 to 0 °C; base, *N*-methylmorpholine, aniline, or *N,N*-dimethylaniline), even trisulfanes with unsaturated (e.g., allyl) or functionalized substituents with –OH, –NH₂, or –COOH groups may be prepared in this way.³⁴

3. Reaction of Sulfenyl Halides with H₂S, H₂S₂, or Their Salts

Aryl- and alkyl-tri- and -tetrasulfanes may be obtained in good yields by reactions of the type shown in eq 18.^{5,7} 2-Nitrophenylsulfenyl bromide or related RSBr compounds react at 20 °C in benzene with HgS , PbS , Ag_2S , or Tl_2S to give the corresponding trisulfanes in 80–100% yield.³⁵ Use of H_2S in ether, acetic acid, dioxane, or ethyl acetate afforded the trisulfanes in lower yields.³⁵ Liquid CCl_3SCl reacts in low yield with H_2S at 20 °C to $(\text{CCl}_3)_2\text{S}_3$ and with H_2S_2 at 85 °C to $(\text{CCl}_3)_2\text{S}_4$; both compounds form colorless crystals.³⁶

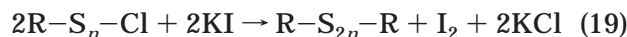


Bis(alkoxycarbonyl)polysulfanes ($n = 3, 4$) have been prepared from the sulfenyl chlorides $\text{RO}-\text{C}(\text{O})-\text{SCl}$ with H_2S_x ($x = 1, 2$) or Na_2S_x ($x = 1, 2$).²² However, reaction 18 does not always proceed in a clean way to give the tri- or tetrasulfane in high yield but, due to secondary interconversion reactions catalyzed by SH compounds or sulfide ions (Section V.D), results in complex mixtures of polysulfanes R_2S_n . These may be separated by LC³⁷ or HPLC;²² see Section IV.C.

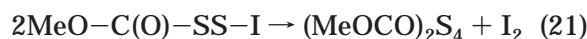
The bifunctional sulfenyl chloride $\text{ClS}-\text{C}(\text{O})-\text{O}-(\text{CH}_2)_4-\text{O}-\text{C}(\text{O})-\text{SCl}$, dissolved in chloroform, reacts with aqueous Na_2S or Na_2S_2 at 20 °C to give the corresponding polymers of general formula $[-\text{S}_n-\text{CO}_2-(\text{CH}_2)_4-\text{CO}_2-\text{S}-]_x$;³⁸ see also Section VII.A.

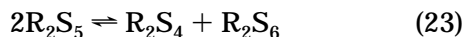
4. Reaction of Sulfenyl Chlorides with Ionic Iodides

Alkoxy carbonyl sulfenyl chlorides react at 20 °C with aqueous potassium iodide primarily with halogen exchange. But since the sulfenyl iodides RSI are unstable, they combine in a bimolecular reaction to give the disulfane and elemental iodine (eq 19). The iodine is removed by washing the organic phase with aqueous sodium thiosulfate:²²



If organochlorodisulfanes RSSCl dissolved in dichloromethane are used, the product of reaction 19 should be the corresponding tetrasulfane. However, due to secondary interconversion reactions (see Section V.A), possibly catalyzed by molecular iodine, a mixture of polysulfanes is obtained:²²

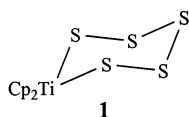




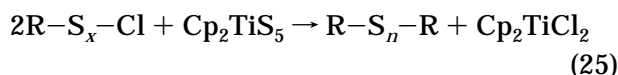
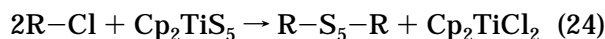
Therefore, depending on the reaction conditions, either the trisulfane or the tetrasulfane was isolated as the main product.^{22,33} The aqueous solution of NaI and Na₂S₄O₆ formed in reaction 20 may be used for another halogen exchange reaction of the type shown in eq 19.³⁹

5. Reaction of Organic Halides or Sulfenyl Chlorides with Titanocene Polysulfido Complexes

The recent preparation of soluble polysulfido complexes of certain metals has tremendously stimulated the investigation of sulfur-rich compounds since these compounds may be used as sulfur transfer reagents.⁴⁰ The mild reaction conditions allow the preparation of even rather sensitive sulfur-rich compounds. Titanocene dichloride Cp₂TiCl₂ reacts with alkali polysulfides to give the chelate complex **1**,⁴¹ from which the dinuclear derivative **2**⁴² can be obtained by desulfurization with triphenylphosphane; the pentasulfide **1** is commercially available (Cp = C₅H₅; Cp' = MeC₅H₄).



These complexes are air-stable and soluble in organic solvents. They react with inorganic sulfur chlorides S_xCl₂ to give homocyclic S_n molecules.⁴³ Analogously, organic sulfenyl chlorides and certain organic halides such as Ph₃CCl react with **1** or **2** as shown in eqs 24–26. These ligand transfer reactions are carried out at temperatures of between 0° and 20 °C in solvents such as CS₂ or CH₂Cl₂ and often take place quantitatively:

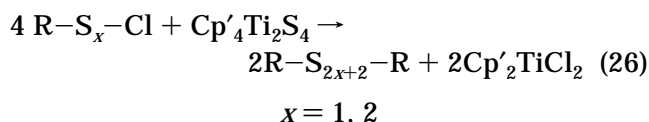
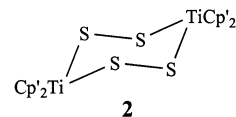


$$x = 1, 2; \quad n = 2x + 5$$

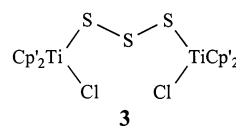
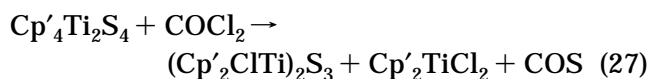
Bis(triphenylmethyl)pentasulfane was obtained in 83% yield from Ph₃CCl and Cp₂TiS₅ in CS₂ at 20 °C.⁴⁴ In an analogous manner, triphenylmethanesulfenyl chloride and the corresponding chlorodisulfane RSSCl react with Cp₂TiS₅ to give the expected hepta- and nonasulfanes, R₂S_n (n = 7, 9).⁴⁵ From CCl₃SCl and **1**, the crystalline heptasulfane (CCl₃)₂S₇ (mp 38 °C) was obtained in 56% yield.⁴⁶ These reactions and the workup procedure can be most conveniently followed by HPLC analysis; see Section IV.C.

The dinuclear complex Cp'₄Ti₂S₄ **2** reacts as a transfer reagent for S₂ units. Therefore, sulfenyl chlorides such as CCl₃SCl yield the corresponding tetrasulfane.⁴⁶ With certain organochlorodisulfanes RSSCl, one obtains the related hexasulfanes R₂S₆ (e.g., R = Ph₃C) (eq 26).^{45,47} The Cp' ligand (η⁵-

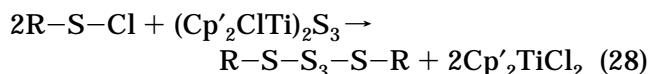
MeC₅H₄) is used because it results in a higher solubility of the dinuclear complex.



A reagent for the transfer of S₃ units can be obtained from the dinuclear complex **2** by reaction with either phosgene or thiophosgene.⁴⁸



The reagent **3** was used, for instance, to prepare di-*n*-octylpentasulfane in high yield according to eq 28.⁴⁹

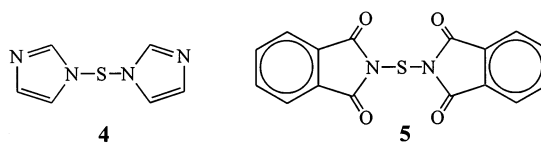


Similarly, cyclic pentasulfanes are obtained if bis-sulfenyl chlorides R(SCl)₂ are employed; see Section II.B.8.

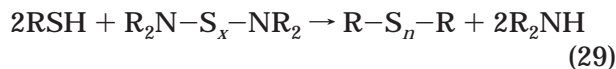
In general, the use of titanocene polysulfide complexes is the preferred method if sulfur-rich organic polysulfanes are to be prepared since the mild reaction conditions, including the absence of strong nucleophiles, prevent the products from decomposing as in eqs 22 and 23.

6. Reaction of Thiols with the Sulfur–Nitrogen Bonds in Sulfenamides

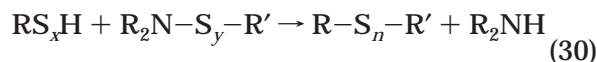
Several sulfenamides and their homologues have been used as transfer reagents for S₁ or S₂ units as shown in eqs 29 and 30. Examples are the bis(imidazolo)sulfane **4** and the bis(phthalimido)sulfane **5**.⁷



These compounds with one or two sulfur atoms bridging the nitrogen atoms may be prepared from the NH derivatives and SCl₂ or S₂Cl₂ in a molar ratio of 2:1 in the presence of a tertiary amine. When SCl₂ is applied in a molar ratio of 1:1, the sulfenyl chloride R₂N-SCl may be isolated, from which the unsymmetrical sulfenamide needed in eq 30 is prepared by condensation with a second thiol R'SH. Alternatively, R₂NSSR' may be prepared from R₂NH and R'SSCl.^{30,50}



$$n = x + 2$$

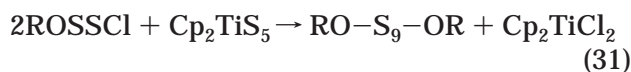


$$x = 1, 2; \quad y = 1, 2; \quad n = x + y$$

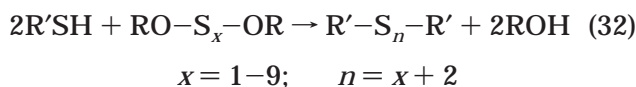
Symmetrical and unsymmetrical tri- and tetrasulfanes may be synthesized by reactions 29 and 30 in high yield and under mild conditions (benzene, 20 °C). Since phthalimide is insoluble in benzene, it is simply filtered off.^{30,50,51} This method has also been applied in the synthesis of peptide trisulfanes.⁵² Various other azole derivatives have been used successfully.⁵³

7. Reaction of Thiols with Bis(Alkoxy)sulfanes

Bis(alkoxy)sulfanes $(\text{RO})_2\text{S}_n$ are easily accessible from the corresponding alcohols by reaction with the sulfenamides **4** or **5**, or with the corresponding dichlorosulfane.^{54,55} Using titanocene pentasulfide **1** as a sulfur transfer reagent and ROSSCl as the alkoxy derivative, a chain length of $n = 9$ in $(\text{RO})_2\text{S}_n$ ($\text{R} = i\text{-Pr}$) has been achieved:⁵⁵

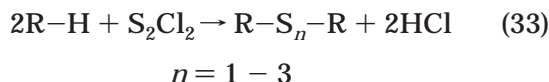


Compounds of the type $(\text{RO})_2\text{S}_n$ react with certain thiols at 20 °C according to eq 32, allowing the preparation of sulfur-rich polysulfanes under mild conditions.⁵⁶ Bis(tetraacetylthioglucosyl)polysulfanes with up to 11 sulfur atoms in a chain have been prepared in this way.⁵⁷ The undecasulfane is the longest homoatomic sulfur chain prepared so far as a pure material. Reactions 29, 30, and 32 are typical nucleophilic displacement processes which will be discussed in detail in Section V.D.



8. Reaction of Dichlorodisulfane with Aromatic Ethers

Methoxybenzene (anisole), 1,2-dimethoxybenzene and similar aromatic ethers react with S_2Cl_2 in dry ether or benzene at 0–20 °C within several days to give a mixture of diarylsulfanes R_2S_n with $n = 1-3$ (eq 33). Anisole is substituted in the para position:⁵⁸



9. Reactions of Organic Halides, Thiols, Sulfonyl Chlorides or Disulfanes with Sulfur Donors Like Elemental Sulfur or Inorganic Polysulfides⁷

Alkyl chlorides, -bromides, and -iodides may be converted to tri- or tetrasulfanes by treatment with elemental sulfur at 20 °C in the presence of KOH and traces of H_2O . Methyl-, ethyl-, isopropyl-, and allyl-polysulfanes have been prepared in this manner.⁵⁹ Sometimes hydrazine is added to reduce S_8 to polysulfide anions which are more reactive.⁶⁰ The reaction

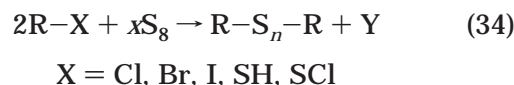
of alkylbromides and -iodides with elemental sulfur to give tri- and tetrasulfanes is promoted by a mixture of tin(II) chloride and copper(II) chloride in THF–DMSO (2:1 v/v). In this way diallyltri- and -tetrasulfane as well as other polysulfanes have been synthesized at temperatures of between 20 and 70 °C.⁶¹

Bromobenzene and other arylbromides react with elemental sulfur at 220–240 °C to give S_2Br_2 and mixtures of polysulfanes,⁶² but no separation of these products has been reported.

Trifluoroiodomethane CF_3I when heated with elemental sulfur to 310 °C in a steel autoclave yields a mixture of $(\text{CF}_3)_2\text{S}_2$ (yield 75%), $(\text{CF}_3)_2\text{S}_3$ (12%), and $(\text{CF}_3)_2\text{S}_4$ (1%).⁶³ Presumably, CF_3 radicals are primarily formed which attack the reactive sulfur molecules present in elemental sulfur at 310 °C.⁶⁴

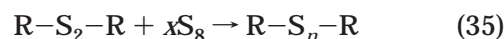
Bis(4-methyl-2-nitrophenyl)trisulfane is formed in 84% yield on reaction of 4-chloro-3-nitrotoluene with molten sodium polysulfide.⁶⁵ Other arylhalides have also been converted to trisulfanes by ionic polysulfides.⁶⁶ The reaction of organic chlorides with sodium polysulfide may be carried out in H_2O /butanone mixture at 75 °C using a phase-transfer catalyst like dodecyltributylphosphonium chloride.⁶⁷

Alkyltri- and -tetrasulfanes may be conveniently prepared from thiols and elemental sulfur in the presence of catalytic amounts of n -butylamine at 25–63 °C according to eq 34, with $\text{Y} = \text{H}_2\text{S}$. The molar ratio $\text{RSH}:\text{S}_8$, the polarity of the solvent (CH_2Cl_2 or MeOH), the reaction time, and the temperature determine the products formed;⁶⁸ n -, i -, and t -alkanethiols as well as cyclo-alkanethiols have been applied:^{68–70}



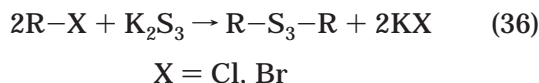
The reaction of n -octane-1-thiol with liquid sulfur at 135–155 °C has been studied kinetically using HPLC analysis of the products.⁷¹ This reaction yields polysulfane mixtures with $n = 2-11$, but the formation of the disulfane is delayed compared to the more sulfur-rich species which form first. Presumably, the initial reaction is the ring opening by the thiol resulting in organylpolysulfanes RS_xH , which then decompose by intermolecular condensation with elimination of H_2S .

Trichloromethanesulfonyl chloride reacts with elemental sulfur at 220 °C to give $(\text{CCl}_3)_2\text{S}_2$ and S_2Cl_2 ; the disulfane may be converted to $(\text{CCl}_3)_2\text{S}_3$ by reaction with sulfur at 170 °C (eqs 34 and 35).⁷² Alkyltrisulfanes have also been prepared from disulfanes and elemental sulfur with addition of H_2S and butylamine, triethylamine, or P_4S_{10} .⁷



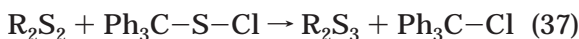
Diethylpentasulfane may be prepared from the trisulfane by heating with elemental sulfur to 200 °C followed by distillation in vacuo.¹⁴ Tetramethylthiuram polysulfanes are formed if the corresponding disulfane (TMTD, a vulcanization accelerator) is heated with sulfur to 130–150 °C to simulate the conditions of the vulcanization of rubber with sulfur;⁷³ see Section VII.B.

The preparation of organic trisulfanes from alkylhalides and alkali trisulfides takes place according to eq 36:^{14,70,74}



In an analogous manner, sodium tetrasulfide, prepared from the elements in dimethoxyethane at 70 °C, reacted at room temperature with aliphatic halides such as benzyl chloride, isopropyl bromide, and 3-(triethoxysilyl)propyl chloride to give mixtures of the corresponding polysulfanes R₂S_n with n = 2–8.⁷⁵

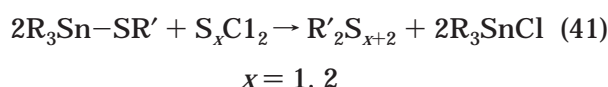
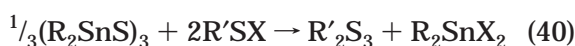
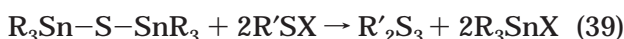
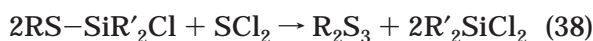
To synthesize trisulfanes with functionalized organic substituents such as -CH₂CH₂OH, the commercially available sulfur atom transfer reagent Ph₃CSCl may be used; the reaction according to eq 37 takes place in chloroform at room temperature within ca. 2 h (yields 42–88%).⁷⁶



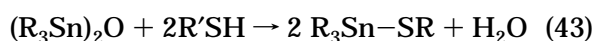
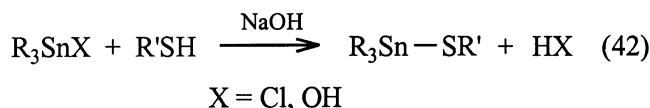
If organic di-, tri-, or tetrahalides are treated with alkali polysulfides, polymeric polysulfanes are obtained; see Section VII.A.

10. Organosilicon and Organotin Reagents for Sulfur Transfer Reactions

Silicon, germanium, and tin are known for their high affinity for chlorine and bromine which is utilized in the reactions shown in eqs 38–41, X = Cl, Br:^{77–79}

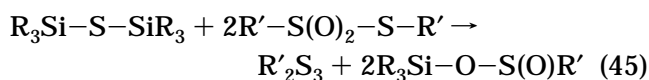
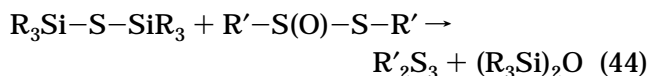


Diethyltrisulfane has been obtained in 87% yield from (ethylthio)dimethylchlorosilane and SCl₂ at 20 °C (no solvent), followed by vacuum distillation (eq 38).⁷⁷ Symmetrical diaryltri- and -tetrasulfanes may be prepared from triorganotin sulfides or thiolate complexes, as shown in eqs 39–41.^{78,80} These reactions proceed smoothly in CHCl₃ or CCl₄ at 20 °C or slightly elevated temperatures. The products are obtained in yields of between 25% and 90%.^{78,79} The organotin thiolates are prepared from R₃SnCl, R₃-SnOH, or (R₃Sn)₂O by reaction with the corresponding thiols:⁷⁹



Silicon is one of the most oxophilic elements. Therefore, organosilicon sulfides reduce certain sulfoxides

and sulfones to sulfanes; however, the chain length of the polysulfane is simultaneously enhanced by one S atom, as shown in eqs 44 and 45:⁸¹

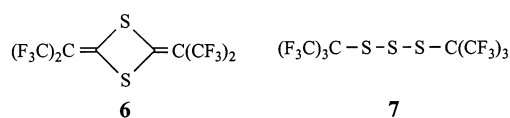


Bis(trimethylsilyl)sulfide reacts with methyl-, phenyl-, or other thiosulfates (disulfane oxides) R'S(O)-SR' in anhydrous chloroform at 60 °C to give the symmetrical trisulfane and hexamethyldisiloxane; the latter and the solvent are removed by vacuum distillation, leaving almost pure R'₂S₃ (yields 70–90%).⁸¹ In a similar reaction, EtSO₂-SEt was converted to Et₂S₃ in 95% yield by the reaction shown in eq 45.⁵⁰

11. Reaction of Alkenes with Elemental Sulfur or Sulfur-Rich Compounds

The reaction of alkenes with elemental sulfur is of tremendous importance because of its analogy to the vulcanization of natural or synthetic rubber by sulfur in the presence of various catalysts. This industrial process and the related model reactions of simple alkenes with sulfur are described in Section VII.B.

Sulfur may react with alkenes either by addition to the C=C double bond or by substitution of H by S with elimination of H₂S. In both cases polysulfanes are formed. Octafluoroisobutene, (CF₃)₂C=CF₂, reacts with elemental sulfur at 60–70 °C in DMF and in the presence of cesium fluoride to give the thioetene dimer **6** and the trisulfane **7** (yields 21% and 35%, respectively, based on alkene). Use of KF instead of CsF also produced some tetrasulfane analogous to **7**.⁸²

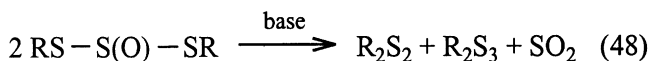
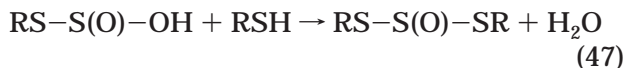
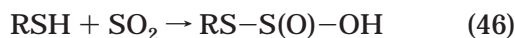


Acrylonitrile CH₂=CH-CN reacts with elemental sulfur at 80 °C in DMF in the presence of NH₃ to give 1,7-dicyano-3,4,5-trithiaheptane (NC-C₂H₄)₂S₃ in 49% yield.⁷⁴ The latter compound may be converted to the dicarbonic acid (HOOC-C₂H₄)₂S₃ by hydrochloric acid (90% yield).⁷⁴ Tetrafluoroethene C₂F₄ was sulfurized by reaction with solid S₈[AsF₆]₂ at 20 °C; after 2 days, AsF₃ and a mixture of polysulfanes of the type (C₂F₅)₂S_n, with n = 2 (80%), 3 (19%), and 4 (0.5%), had formed.⁸³

2,3-Dimethylbutadiene reacts with sulfanes H₂S_n (n = 4–7) in CS₂ at 10 °C to the corresponding bis-(2,3-dimethyl-2-butene-1-yl)polysulfanes, which can also be obtained by heating tetramethylethene and elemental sulfur in the presence of zinc oxide and an accelerator like tetramethyldiuram disulfane.⁸⁴ These reactions are of interest in connection with the mechanism of rubber vulcanization by sulfur; see Section VII.B.

12. Reaction of Thiols with Sulfur(IV) and Sulfur(VI) Compounds (SO₂, Tetrahalides, Thioisulfates, Sulfinyl Imides, Bunte Salts)

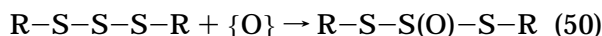
Thiols are powerful reducing agents which may be oxidized by O₂, peroxides, halogens, sulfoxides, or metal ions in high oxidation states [e.g., FeCl₃, Pb(OOCMe)₄]; usually disulfanes are formed in these reactions.^{5,7} Oxidation of thiols by sulfur(IV) or sulfur(VI) compounds often results in mixtures of polysulfanes. Liquid SO₂ oxidizes alkanethiols in the presence of triethylamine at 20 °C to a mixture of di- and trisulfanes (ratio ca. 7:3):⁸⁵



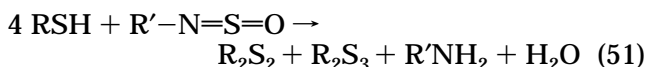
The postulated intermediates RS-S(O)-OH and R₂S₃O have not been observed. However, trisulfane 2-oxides (RS)₂SO are known from the reaction of thiols with thionyl chloride in the presence of a weak base:⁸⁶⁻⁸⁹



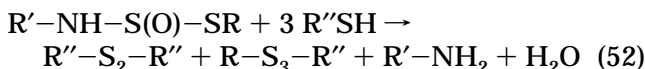
Oxidation of trisulfanes by peroxy compounds sometimes also produces trisulfane 2-oxides (see Section V.E).



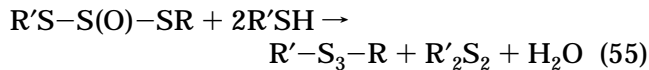
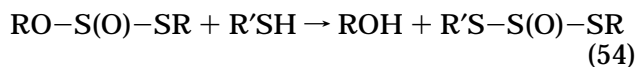
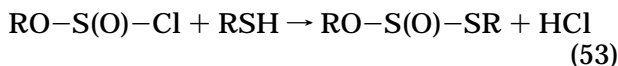
N-Sulfinylimides oxidize substituted aromatic thiols to yield equimolar mixtures of di- and trisulfanes:



This reaction proceeds via the intermediate "adduct" R'-NH-SO-SR **8** which can be isolated in favorable cases (e.g., with R' = 4-NO₂C₆H₄).⁹⁰ Compound **8** reacts with thiols according to eq 52, allowing the preparation of symmetrical disulfanes and asymmetrical trisulfanes:



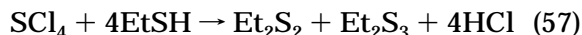
Since the sulfinyl imide **8** does not have to be isolated, the reaction of *N*-phenylsulfinyl imide with benzenethiol at -15 °C in ether followed by addition of ethanethiol in acetone resulted in Et-S₃-Ph, which was isolated in 24% yield.⁹⁰ Other alkylaryltrisulfanes have been prepared by analogous reactions. The reaction of alkoxythionyl chloride with thiols proceeds also via reactive intermediates and is therefore useful for the preparation of asymmetrical trisulfanes according to eqs 53-55, with R = alkyl and R' = aryl:⁹⁰



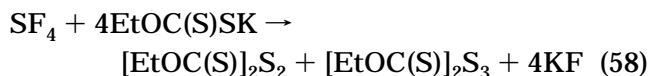
The reduction of trisulfane 1-oxides, R-S(O)-S-S-R, by thiols R'SH results in asymmetrical di- and trisulfanes:⁹¹



Sulfur tetrachloride SCl₄ and ethanethiol react at -20 °C or below in ether according to eq 57⁹² since the expected tetrathiosulfurane (RS)₄S is unstable and has never been observed:⁹³

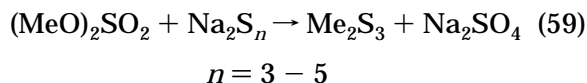


However, since SCl₄ easily decomposes to SCl₂ and Cl₂, the observed products most likely originate from the reaction of the thiol with the dissociation products of SCl₄. In a seemingly similar reaction, SF₄ and potassium ethyl xanthate yield the corresponding di- and trisulfanes in benzene at 20 °C:²⁶

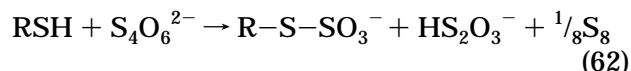
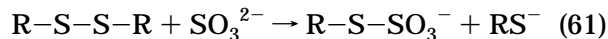
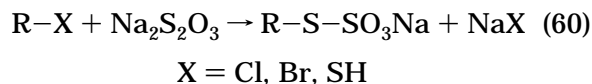


13. Reaction of Inorganic Polysulfides with Organic Sulfur-Oxygen Compounds (Thioisulfates, Bunte Salts, Dimethyl Sulfate)

Dimethyl sulfate is a strong methylating agent which reacts at 20 °C with alcoholic solutions of sodium polysulfides to give mixtures of dimethylpolysulfanes from which Me₂S₃ may be obtained in 80% yield by distillation.^{14,94}



Organic thioisulfates RSSO₃M (M = Na, K, etc.) are called Bunte salts and may be obtained either from organic halides or thiols with aqueous thioisulfate, by cleavage of disulfanes with sulfite ions, or by reaction of thiols with tetrathionate ions:^{95,96}

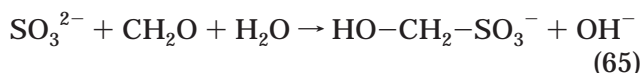


Bunte salts react with aqueous sulfide under mild conditions to give trisulfanes in high yield:



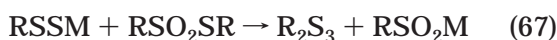
Trisulfanes with R = methyl, ethyl, allyl, benzyl, phenacyl, 4-tolyl, and 2-methylpent-2-enyl have been

prepared in this way. The pH of the solution is kept at 8 using a buffer, and the trisulfane is extracted by ether or hexane.^{66,96} To prevent the sulfite ions liberated in reactions 63 and 64 from attacking the trisulfane with formation of disulfane and thiosulfate, the reaction is carried out in the presence of an excess of formaldehyde, which at pH 8 traps the sulfite:

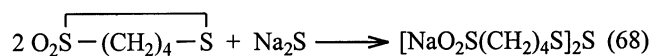


In addition, saturation of the aqueous phase with NaCl lowers the solubility of R₂S₃ which is then more rapidly extracted into the organic phase.⁹⁶

Thiosulfonates R-SO₂-S-R (disulfane 1,1-dioxides) are thioalkylating agents since the S-S bond is weak and easily cleaved. Therefore, sulfide ions react with thiosulfonates in a similar fashion as Bunte salts (see above), and symmetrical alkyl- and aryltrisulfanes may be prepared in high yields by reactions 66 and 67:³⁷



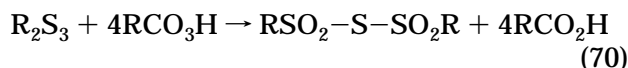
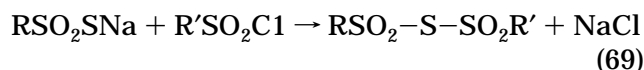
The reaction is carried out in methanol at 20 °C. It is obvious from eqs 66 and 67 that the central sulfur atom of the trisulfane originates from the sulfide. Cyclic thiosulfonates result in chain-like trisulfanes with chain-terminating SO₂⁻ groups (eq 68, yield 70%).⁹⁷



Sulfinate compounds of this type are water soluble and may be used as antiradiation drugs (see Section VII.D).⁹⁷⁻⁹⁹ Bis(sulfinato)trisulfanes may be converted to the corresponding dialkylesters by reaction with either diazomethane or a solution of BF₃ in diethyl ether.¹⁰⁰ When sodium polysulfide is applied in eq 66, the resulting polysulfanes according to eq 67 contain up to six sulfur atoms. However, the bis(sulfinato)polysulfanes with more than four catenated sulfur atoms are unstable in water, and elemental sulfur is slowly precipitated.⁹⁸ When the thiosulfonate RS(O)-(CH₂)₂-SSO₂C₆H₄Me was used in reactions 66 and 67, the bis(sulfoxido)trisulfane [RS(O)-(CH₂)₂]₂S₃ resulted.⁹⁹

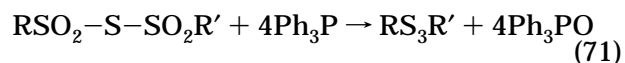
14. Reduction of Sulfane Oxides by Triphenylphosphane

Trisulfane 1,1,3,3-tetroxides RSO₂-S-SO₂R may be prepared by reaction 69¹⁰¹ or by oxidation of trisulfanes with peroxo acids, eq 70:¹⁰²



Triphenylphosphane is an oxophilic compound which reduces sulfoxides R₂SO, disulfane oxides RS-

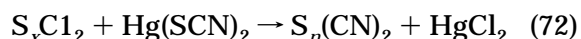
(O)SR, and disulfane dioxides RSO₂SR as well as trisulfane tetroxides to the corresponding sulfanes. From the products prepared by reactions 69 or 70, symmetrical or asymmetrical aryl- or alkyltrisulfanes are obtained in high yield (refluxing in ether or benzene).¹⁰¹



Sulfoxides are intermediates in reaction 71. An excess of Ph₃P converts the trisulfanes via disulfanes to monosulfanes R₂S; see Section V.D.¹⁰¹

15. Miscellaneous Reactions for the Preparation of Chain-Like Polysulfanes

Dicyanosulfanes S_n(CN)₂ with n = 3-9 have been prepared by reaction of the corresponding dichlorosulfanes with Hg(SCN)₂ in CS₂, sometimes in the presence of some EtBr as a polar solvent.¹⁰³⁻¹⁰⁵



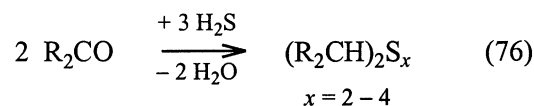
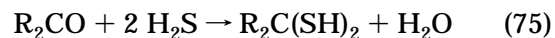
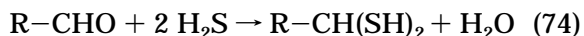
The insoluble HgCl₂ and the excess of Hg(SCN)₂ are filtered off. While S₃(CN)₂, S₆(CN)₂, and S₉(CN)₂ are crystalline solids, the other dicyanosulfanes are oily liquids at 20 °C but crystallize on cooling. They precipitate from the filtrate on cooling. The chain-like structures of S_n(CN)₂, with n = 3, 4, 6, 9, have been confirmed by X-ray diffraction on single crystals; see Section III.B.

Bis[tris(trimethylsilyl)methyl]trisulfane was obtained by lithiation of the sterically demanding substituents (Me₃Si)₃CH with MeLi in THF and reacting the product with elemental sulfur, followed by oxidation with gaseous O₂ (yield 45%).¹⁰⁶

Aliphatic acid chlorides react with trisulfane H₂S₃ in the presence of ZnCl₂ at 20 °C (no solvent) according to eq 73:²¹



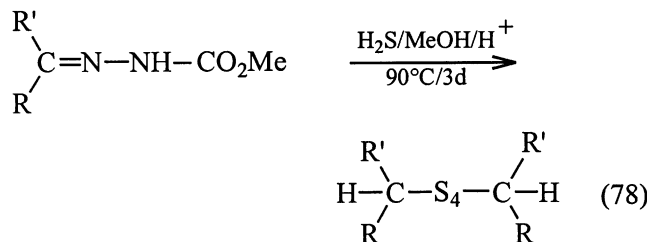
Aliphatic ketones and aldehydes if treated with H₂S at high pressure give a mixture of geminal dithiols and tri- and tetrasulfanes according to eqs 74-76.¹⁰⁷



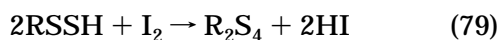
Polysulfane yields of up to 60% (applying to the mixture) were obtained. From acetylacetone, a cyclic trisulfane was prepared.¹⁰⁷

Primary and secondary dialkyltetrasulfanes may be prepared from ketones via hydrazones by reaction with H₂S (eqs 77 and 78).¹⁰⁸ The mechanism and stoichiometry of reaction 78 are unknown, but probably MeCOOH and 2 NH₄⁺ are formed as byproducts,

in which case four equivalents of H₂S are needed, resulting in a tetrasulfane:

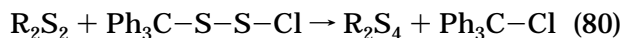


Oxidation of organyldisulfanes RSSH by iodine in ethanol according to reaction 79 or by quinones in benzene affords tetrasulfanes in high yield:⁷

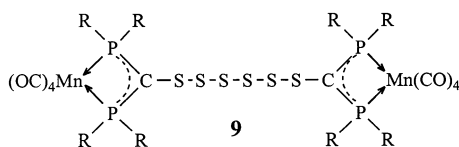


Carbon disulfide reacts with iodine pentafluoride in a sealed tube at 195 °C to give a mixture of CF₄, SF₄, (CF₃)₂S₂, (CF₃)₂S₃, and probably I₂. The trisulfane was isolated in 7% yield by vacuum distillation.⁶³ Bis-(perchloroethyl)tetrasulfane (C₂Cl₅)₂S₄ was obtained in 8% yield from C₂Cl₅SSC(O)CH₃ by chlorination in a reaction of unknown mechanism.¹⁰⁹

Dialkyltetrasulfanes were obtained in 71–97% yield from the corresponding disulfanes by treatment with Ph₃CSSCl as a transfer reagent for S₂ units:¹¹⁰



Manganese complexes containing anionic polysulfane ligands of the type [(PPh₂)₂C-S_n-C(PPh₂)₂]²⁻, with *n* = 2 and 6, have been prepared by nucleophilic degradation of S₈ by the methanide complex [Mn(CO)₄{(PPh₂)₂CH}] in dichloromethane solution at 20 °C.¹¹¹ At each end of the bridging ligand, two phosphorus atoms coordinate to one Mn(CO)₄ unit as shown in the case of **9**.



Both complexes were characterized by X-ray crystallography of single crystals. Desulfurization of the hexasulfane by triphenylphosphane gave mixtures of the corresponding tri-, tetra- and pentasulfanes.

B. Cyclic Organic Polysulfanes

1. Nomenclature

For the nomenclature of organic rings, the Hantzsch-Widman system is normally used, which indicates the ring size by specific suffixes as follows. The first suffix given is used in the case of saturated, the second in the case of unsaturated rings:

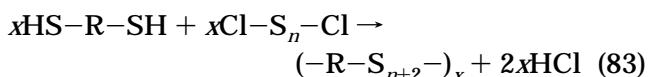
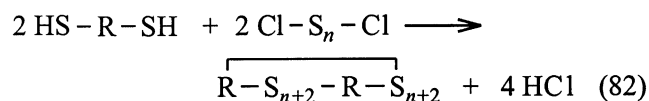
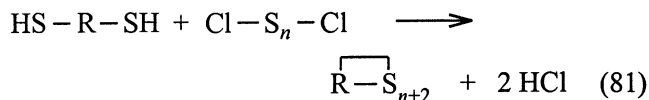
- (i) three-membered rings: -irane, -iren
- (ii) four-membered rings: -etane, -ete
- (iii) five-membered rings: -olane, -ole

- (iv) six-membered rings: -ane, -in
- (v) seven-membered rings: -epane, -epin
- (vi) eight-membered rings: -ocane, -ocin
- (vii) nine-membered rings: -onane, -onin
- (viii) ten-membered rings: -ecane, -ecin

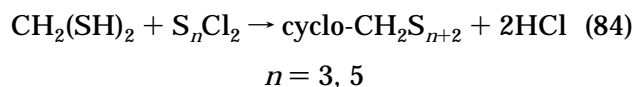
Examples will be presented in the following sections.

2. Reaction of Dithiols with Dichlorosulfanes

The reaction of organic dithiols with dichlorosulfanes may result in the formation of rings, of oligomeric rings, or of polymers by reactions shown in eqs 81–83:



The formation of small rings according to eq 81 is promoted by the application of the dilution principle (simultaneous addition of both reagents to a large volume of solvent to keep the actual concentration low). Nevertheless, if the size of the wanted ring is too small (<6), the dimeric compound will form either exclusively or in addition to the monomeric ring (eq 82). These reactions often are carried out in ether, which binds the HCl byproduct by strong hydrogen bonds. On the other hand, a hydrocarbon solvent, together with a tertiary amine added in stoichiometric amounts, may be used also. Rings with up to seven neighboring sulfur atoms have been synthesized by reaction 81. Methanedithiol reacts with S₃Cl₂ to give pentathiane CH₂S₅ and with S₅Cl₂ to heptathiacyclooctane CH₂S₇ (eq 84). Both compounds form yellow crystals,¹¹² the structures of which have been determined by X-ray diffraction; see Section III.C.



Substituted methanedithiols react with S₃Cl₂ also according to eq 84.¹¹³ However, when methanedithiol or substituted derivatives are reacted with SCl₂, an eight-membered cyclic bis-trisulfane rather than a four-membered ring is obtained (eq 82, with *n* = 1).¹¹³

Numerous aliphatic and aromatic dithiols have been treated with dichlorosulfanes, and cyclic polysulfanes have been obtained in yields of up to 80%.^{114–117} Sometimes the sodium salt of the dithiol is used,¹¹⁸ in which case the ring size obtained may be different from what is expected since the strongly nucleophilic RS⁻ ions catalyze secondary interconversion reactions; see Section V.A.

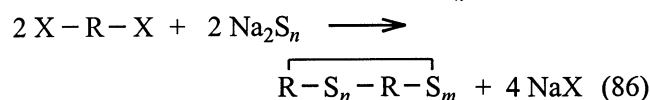
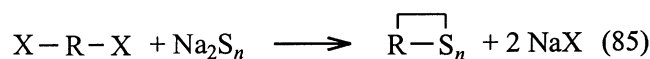
Despite the high reactivity of dichlorosulfanes toward C=C double bonds, it is possible to synthesize

cyclic organic polysulfanes with alkenic double bonds by reaction 81, for example, isothiazolepentasulfane,¹¹⁸ pentathiepin C₂H₂S₅,¹¹⁹ norbornene pentasulfane C₇H₈S₅,¹¹⁹ and dicyclopentadiene tetrasulfane C₁₀H₁₂S₄.¹²⁰ 3,6-Dimercapto-1,4-dimethyl-2,5-dioxopiperazine reacts with S₂Cl₂ without a base to a stable bicyclic tetrasulfane,¹²¹ which is related to the naturally occurring antibiotic polysulfanes gliotoxin, sporidesmin, aranotin, and chaetocin II; see Section VI.B.

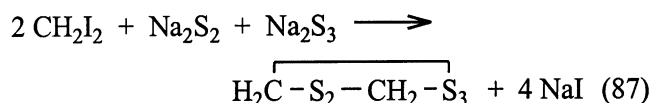
Bicyclic pentathiepins have been obtained from the reactions of vicinal dithiols such as cyanoisothiazol-3,4-dithiol, thiophene-3,4-dithiol, and benzodithiol with S₂Cl₂ rather than S₃Cl₂.¹²² Obviously, some sulfur transfer reactions are taking place between unknown intermediates of these reactions.

3. Reaction of Bifunctional Organic Halides, Tosylates, or Esters with Sodium Polysulfides

The reactions depicted in eqs 85 and 86 are similar to those shown in eqs 81–83: depending on the size of the organic group R and on the polysulfide anion S_n²⁻, either a small ring or a larger ring as shown in eq 86 will form. Since aqueous polysulfide consists of various homologous anions in equilibrium, the resulting polysulfanes may contain several different S_n units. The strongly nucleophilic polysulfide ions substitute the halide ions Cl⁻, Br⁻, or I⁻, the tosylate anion MeC₆H₄SO₃⁻, or the alcoholate anion RO⁻:



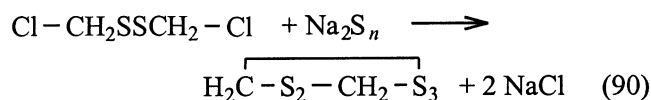
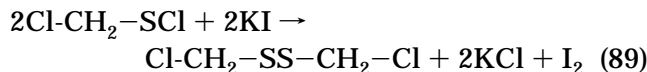
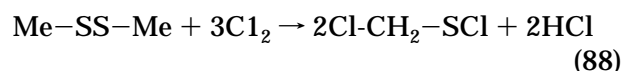
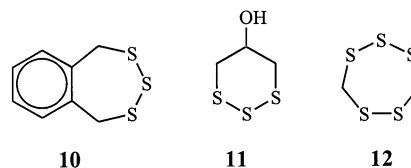
Aqueous sodium polysulfide of average composition Na₂S_{2.5} reacts at 20 °C with diiodomethane within 5 h to 1,2,3,5,6-pentathiacycloheptane **12** (trivial name, lenthionine; see Section VI.C), which is extracted into chloroform and purified by LC:¹²³



When an excess of CH₂Cl₂ is stirred with aqueous Na₂S_{2.5} at pH 8, lenthionine and hexathiacycloheptane CH₂S₆ are obtained. The same reaction carried out at pH 12 yields 1,2,4-trithiacyclopentane (trithiolane) and 1,2,4,6-tetrathiacycloheptane (tetrathiepane), which can be separated by vacuum distillation.¹²³

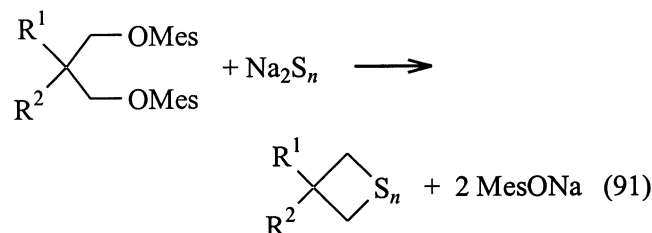
Various aliphatic and aromatic dichlorides and dibromides have been used to synthesize tri- and tetrasulfanes by reaction with aqueous or alcoholic sodium polysulfide. For instance, the benzotrithiepin **10** was obtained from the corresponding dibromide¹²⁴ and hydroxytrithiane **11** from glycerol- α,α' -(dichlorohydrin):¹²⁵

Lenthionine **12** (1,2,3,5,6-pentathiepane) was also obtained from dimethyl disulfane via bis(chloromethyl)disulfane:¹²⁶

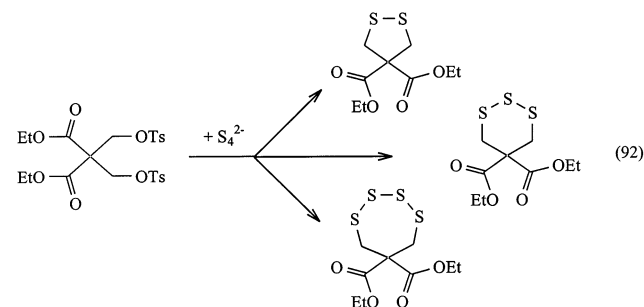


An epitetrasulfane of 2,5-piperazinedione has been prepared from the dibromide and Na₂S_x.¹¹⁹

Bifunctional mesityl ethers react with aqueous sodium polysulfide to give cyclic di- and trisulfanes in high yields:⁷⁴

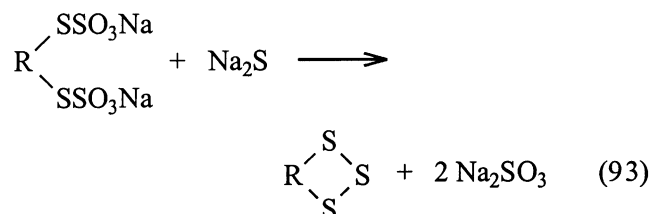


Similarly, bifunctional tosylates yield cyclic di-, tri-, and tetrasulfanes on treatment with sodium polysulfide.¹²⁷



4. Reaction of Organic Thiosulfates (Bunte Salts) or Thiosulfonates with Sodium Sulfide

Bunte salts and thiosulfonates react with aqueous sulfide as shown in eqs 62 and 63. When bifunctional Bunte salts are used, cyclic trisulfanes are obtained:



To prevent the sulfite from attacking the trisulfane (with formation of thiosulfate and disulfane), the reaction is carried out in the presence of formalde-

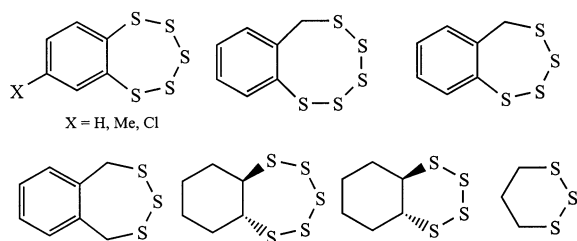
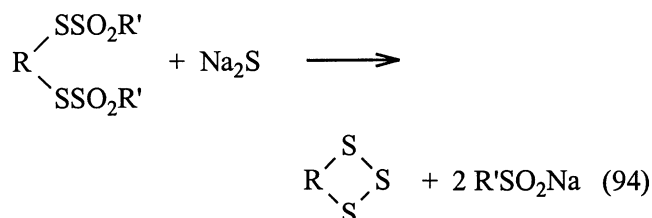


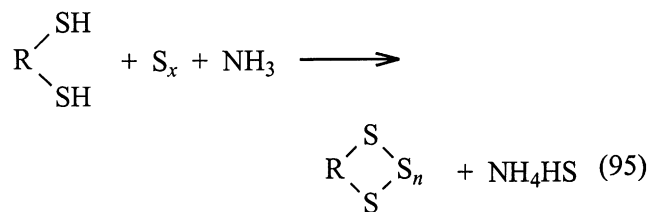
Figure 1. Polysulfanes prepared from dithiols and elemental sulfur in the presence of ammonia as a catalyst.

hyde at pH 7; see eq 65. Aromatic, aliphatic, and alkenic trisulfanes have been obtained in this way in high yields.^{91,128} Bifunctional thiosulfonates react similarly (no CH_2O is needed) and provide cyclic trisulfanes in high yields:⁹¹



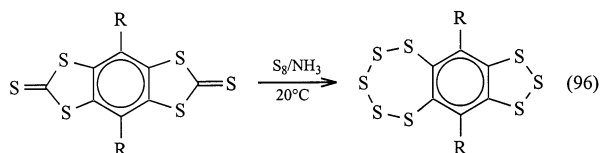
5. Reactions of Dihalides, Dithiols or Thiocarbonates with Elemental Sulfur

Aliphatic and aromatic dithiols react with elemental sulfur in liquid ammonia at 20 °C according to eq 95:^{129,130}

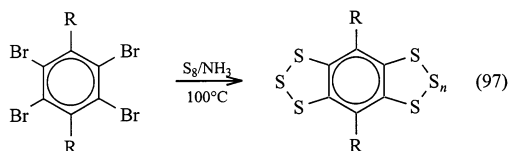


Various cyclic di-, tri-, tetra-, and pentasulfanes have been prepared by the reaction shown in eq 95; examples are given in Figure 1. In some cases the reaction is carried out at room temperature in $\text{CH}_2\text{-Cl}_2$ by bubbling ammonia into the mixture.¹³¹

Aromatic bistrithiocarbonates have been used to synthesize cyclic bis-polysulfanes, as shown in eq 96 ($\text{R} = \text{OMe}, \text{OEt}, \text{O}^i\text{Pr}, \text{OCH}_2\text{Ph}$):^{129,130}



Polycyclic polysulfanes may also be obtained from aromatic tetrahalides, as shown in eq 97 ($\text{R} = \text{Me}, \text{Et}, n = 1, 3$):^{129,130}



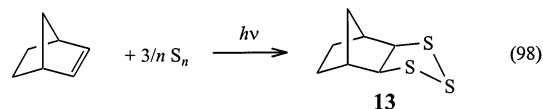
For a recent review on cyclic benzopolysulfanes, see ref 132.

The preparation of 1,2,3-trithiane from $\text{Br}(\text{CH}_2)_3\text{-Br}$ and elemental sulfur in the presence of KOH in THF has been reported.⁵⁹

6. Reactions of Alkenes with Elemental Sulfur

The reactions of sulfur with various types of organic compounds have been reviewed in a monograph in 1987.¹³³

Alkenes and elemental sulfur or sulfur-rich compounds react under certain conditions to yield cyclic polysulfanes. For example, tetrafluoroethylene C_2F_4 reacts with boiling elemental sulfur (445 °C) to tetrafluoro-1,2,3-trithiolane (yield 10%) and tetrafluoro-1,2,3,4-tetrathiane (60%); both compounds are malodorous oils.¹³⁴ Ordinary hydrocarbons would yield H_2S under these conditions; therefore, a catalyst or irradiation is applied to achieve milder reaction conditions. When a mixture of norbornene and S_8 in CS_2 is irradiated (350 nm wavelength), besides other products, the trithiolane derivative **13** is formed (77% yield):¹³⁵



Since irradiation of S_8 in CS_2 results in various reactive sulfur molecules S_n ($n \neq 8$),¹³⁶ it is not clear which molecules S_n are actually reacting in eq 98. Cyclohexene reacts similarly as norbornene.¹³⁵ The trisulfane **13** is also formed when norbornene is heated for 3 h with cyclodecasulfur S_{10} in a toluene/ CS_2 mixture to 90 °C.¹³⁷

Heating of norbornene, dicyclopentadiene (DCPD), or tricyclopentadiene with elemental sulfur in DMF in the presence of NH_3 or triethylamine also produces the corresponding 1,2,3-trithiolane derivatives in yields of 20–85%.¹³⁸ (For the reaction of liquid sulfur with dicyclopentadiene, see also Section VII.C.) A careful investigation of the reactions of sulfur with norbornene, norbornadiene, and dicyclopentadiene showed that the tri- and the pentasulfanes are formed and may be isolated as pure materials; in the case of norbornene, these species are in equilibrium in solution at 20 °C:¹³⁹

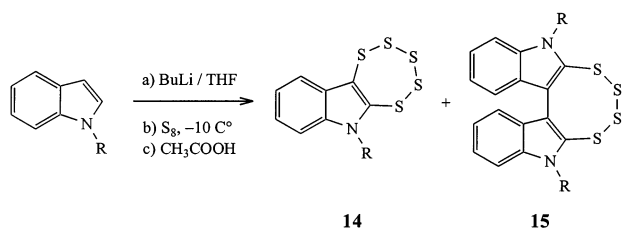


The formation of the cyclic pentasulfane from DCPD can, however, be suppressed by adding Na_2S as a catalyst.¹⁴⁰ The DCPD polysulfanes $\text{C}_{10}\text{H}_{12}\text{S}_n$, with $n = 4-8$, have been independently synthesized from titanocene polysulfides and DCDP sulfonyl chlorides by sulfur transfer reactions;¹²⁰ see Section II.B.8.

Cycloheptatriene reacts with elemental sulfur in sulfolane at 70 °C and in the presence of pyridine in such a way that an S_3 unit is added across the 1,6-positions, resulting in 2,3,4-trithiabicyclo[4.3.1]deca-

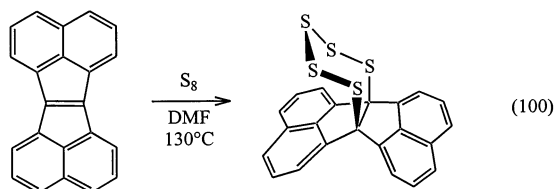
6,8-diene (21% yield).¹⁴¹ Trimethylvinylsilane, Me₃-Si-CH=CH₂, and sulfur react at 55 °C in the presence of Fe₃(CO)₁₂ to give, inter alia, 1-trimethylsilyl-2,3,4,5,6-pentathiacycloheptane.¹⁴² The reaction of alkenes with S₈ to give cyclic trisulfanes has also been carried out by reduction with NaH in toluene in the presence of a phase transfer catalyst.¹⁴³ Indole fused pentathiepins were obtained by lithiation of indole or *N*-methylindole by *n*-BuLi in THF, followed by thionation with an excess of elemental sulfur¹⁴⁴ (Scheme 1, R = H, Me).

Scheme 1

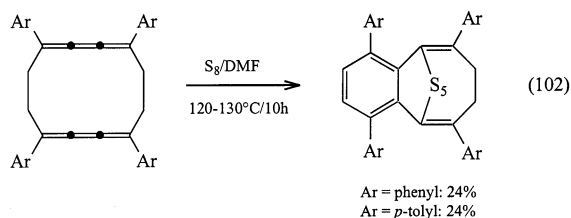
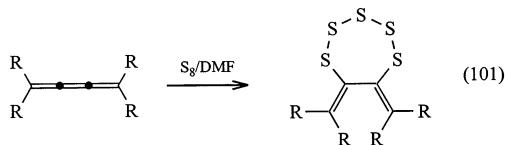


Pentathiepinol[6,7-*b*]indole **14** (R = Me) was obtained in 22% yield and the tetrathiodiindole **15** in 10%. Refluxing of **14** in ethanol in the presence of Et₃N for 30 min resulted in the formation of **15** (89%) and S₈. The pentasulfane **14** is also obtained in low yield on reaction of isatin with P₄S₁₀ in pyridine,¹⁴⁵ while the tetrasulfane **15** is also accessible by reaction of indole with S₈ in dimethylformamide at 145 °C (yield 59%).¹⁴⁶

A pentathiepane was obtained by heating acenaphtho[1,2-*α*]acenaphthylen with S₈ in DMF to 130 °C:¹⁴⁷



Unusual unsaturated cyclic polysulfanes are obtained on reaction of tetraarylbutatrienes with elemental sulfur in DMF at 125 °C:¹⁴⁸



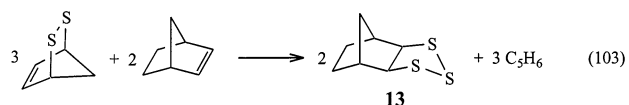
7. Reactions of Alkenes with Sulfur Compounds: Sulfur Transfer Reactions

Formally, the highly reactive S₂ molecule may be generated in solution by various methods.¹⁴⁹ Its

Table 3. Products of the Formal Addition of S₂ to Cyclic Alkenes

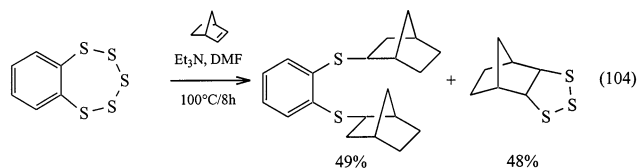
Ene	Product(s)	Yield (%)
		75
		88
		15
		18
		31
		87 / 13

intermediate presence has been deduced from the observation that certain alkenes are turned into disulfanes. However, tri- and tetrasulfanes are sometimes formed in addition. Only the latter reactions will be reported here. 2,3-Dithiabicyclo[2.2.1]hept-5-ene, produced in solution by oxidation of cyclopentene-3,5-dithiol, reacts at 130–160 °C with norbornene C₇H₁₀ to give the trisulfane **13** in 61% yield:¹⁵⁰



The same product **13** is obtained when S₂ is formally generated from (R₃Ge)₂S₃ by reaction with Ph₃PBr₂.¹⁴⁹

Analogously, the enes shown in Table 3 result in the cyclic trisulfanes at the given yields.¹⁴⁹ The exact pathway of these reactions is unknown. The formation of the 1,2,3-trithiolane **13** has also been observed when norbornene was heated with benzopentathiepin 1,2-C₆H₄S₅ in DMF in the presence of triethylamine (yield 48%, temp. 100 °C):¹⁵¹



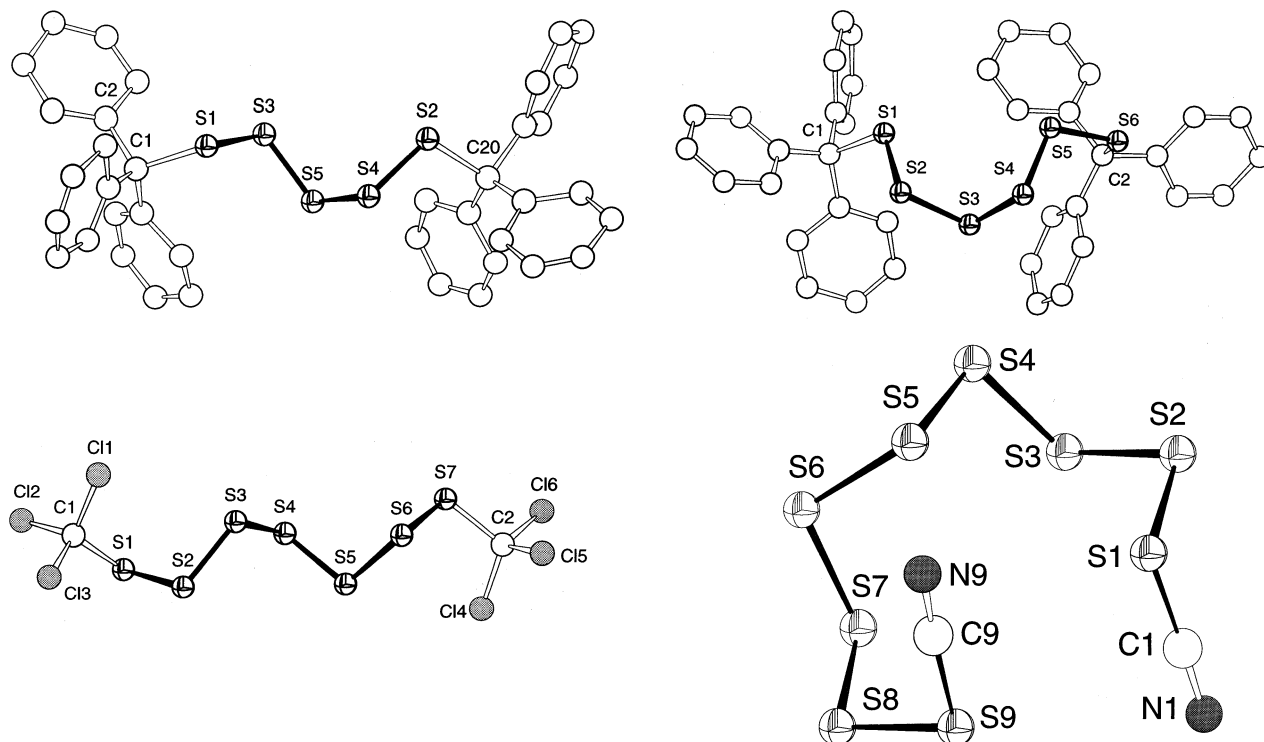
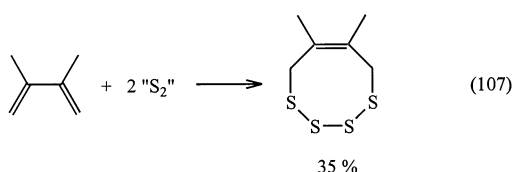
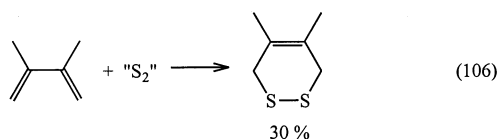
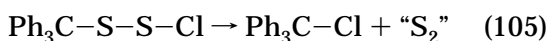


Figure 2. Molecular structures of four chain-like polysulfanes demonstrating the differing motifs: $(\text{Ph}_3\text{C})_2\text{S}_5$ (A), $(\text{Ph}_3\text{C})_2\text{S}_6$ (B), $(\text{CCl}_3)_2\text{S}_7$ (C), and $\text{S}_9(\text{CN})_2$ (D). Hydrogen atoms have been omitted.

The benzopentathiepin on heating in the presence of R_3N seems to split into S_3 and $1,2\text{-C}_6\text{H}_4\text{S}_2$, which are both trapped by the added norbornene.¹⁵¹ The analogous reactions of benzopentathiocin and the related benzoctathiepin with various enes, dienes, and trienes in DMSO have been investigated, and di- or trisulfanes resulting from [2+3], [4+2], or [6+3] cycloaddition reactions were isolated in high yield.¹⁵¹ These remarkable reactions show that cyclic sulfur-rich polysulfanes on heating in polar solvents may produce various reactive sulfur species which can be transferred to suitable alkenic acceptors. If less reactive alkenes such as cyclohexene or cyclooctene are used, elemental sulfur instead of cycloadducts is obtained.¹⁵¹ For S_3 transfer reactions, see also Section V.B.

Triphenylmethylchlorodisulfane reacts with 2,3-dimethyl-1,3-butadiene to give two polysulfanes, both of which seem to arise from the addition of S_2 :¹⁵²

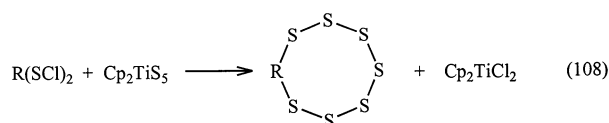


The actual mechanism, however, involves addition of Ph_3CSSCl to the diene with subsequent elimination of Ph_3CCl .¹⁵²

Disulfur may formally be generated by thermal decomposition of dialkoxydisulfanes $(\text{RO})_2\text{S}_2$, which also react with 2,3-dimethyl-1,3-butadiene to the cyclic disulfane 1,2-dithia-4,5-dimethyl-4-cyclohexene, which is further sulfurized to the corresponding tetrasulfane.¹⁵³ It has, however, been observed that elemental sulfur (S_8) also yields the Diels–Alder adduct when heated with 2,3-dimethyl-1,3-butadiene.¹⁵⁴ The formation of this adduct has often been considered as conclusive evidence for the intermediate formation of S_2 . However, this kind of empiricism should be treated with caution and it seems more reasonable to talk about the transfer of S_2 units from the precursor molecule to the acceptor rather than the generation of S_2 as an intermediate.

8. Reactions of Metal Polysulfido Complexes with Bis(Sulfonyl Chlorides)

As already mentioned in Section II.A.5, titanocene pentasulfide **1** has been used extensively as a transfer reagent for the chain-like S_5 unit to prepare numerous inorganic homo- and heterocycles.^{40,43} More recently, cyclic organic polysulfanes have also been obtained from **1** by reaction with bis(sulfonyl chlorides):



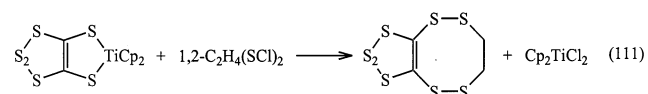
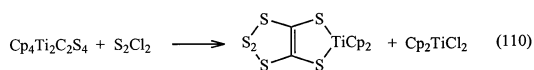
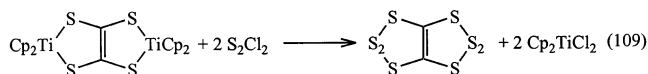
For example, $1,2\text{-C}_2\text{H}_4(\text{SCl})_2$ reacts with Cp_2TiS_5 **1** to give the nine-membered ring $\text{C}_2\text{H}_4\text{S}_7$ in 31% yield.^{44,47} Toluene-1,2-bis(sulfonyl chloride) $\text{MeC}_6\text{H}_3(\text{SCl})_2$ reacts similarly to give the bicyclic $\text{MeC}_6\text{H}_3\text{S}_7$.^{44,47} Norbornanetrithiolan **13** on chlorination gives

one of the two sulfenyl chlorides C₇H₁₀(SCL)₂ or C₇H₁₀(SCL)(SSCL), depending on the reaction conditions. These react with **1** to the polysulfanes C₇H₁₀S₇ and C₇H₁₀S₈, respectively.¹⁵⁵ The dicyclopentadiene (DCPD) polysulfanes C₁₀H₁₂S_n, with n = 4–8, were obtained using the polysulfido complexes Cp₂TiS₅ **1** and (Cp'2-TiCl)₂S₃ **3** as ligand transfer reagents together with the three sulfenyl chlorides C₁₀H₁₂(SCL_m)(S_nCl), with m, n = 1, 2. The latter reagents are obtained partly by chlorination of the trisulfane which is accessible from the reaction of DCPD with elemental sulfur and partly by reduction of the trisulfane to the dithiol and its reaction with SCl₂ or SO₂Cl₂.¹²⁰

Reactions as in eq 108 usually proceed very cleanly and almost quantitatively. The advantage of Cp₂TiS₅ over sodium pentasulfide is not only that it is soluble in organic solvents such as CS₂ and CH₂Cl₂ and does not equilibrate with other ring sizes, but also that it does not introduce nucleophilic polysulfide anions which catalyze decomposition and interconversion reactions of metastable sulfur-rich compounds. Such decomposition reactions are described in Section V.A.

On treatment with acetone and sodium sulfide, Cp₂TiS₅ is transformed to Cp₂Ti(μ-S₂)₂CMe₂,¹⁵⁶ which is also a ligand transfer reagent; it reacts with S₂Cl₂ to dimethylhexathiepin Me₂CS₆ (30% yield) and with a mixture of dichlorosulfanes S_nCl₂ (n = 1–30) to yield the corresponding mixture of sulfur-rich heterocycles Me₂CS_{n+4}, which was analyzed by HPLC. Molecules with up to 35 sulfur atoms in the ring have been detected in this mixture.¹⁹ In a similar fashion, Cp₂TiS₄C₆H₁₀ was obtained from Cp₂TiS₅ and cyclohexanone; on reaction with S₂Cl₂ or S₇Cl₂, this titanocene complex gave the sulfur-rich heterocycles C₆H₁₀S₆ and C₆H₁₀S₁₁, respectively, which contain a spiro carbon atom. According to an X-ray analysis, the conformation of the 12-membered ring in C₆H₁₀S₁₁ (Figure 3) is the same as that in S₁₂.¹⁵⁷

Another valuable titanocene precursor is obtained by action of CS₂ on Cp₂Ti(CO)₂ at 20 °C, resulting in Cp₄Ti₂C₂S₄.¹⁵⁸ This dinuclear complex contains the ligand C₂S₄⁴⁻, which may be utilized to synthesize bicyclic polysulfanes as shown in eqs 109–111.^{159–161}



A similar reaction, shown in eq 112, yielded the novel carbon sulfide C₃S₈ in 15% yield¹⁶² rather than C₃S₇, which might have been expected from the reactants:

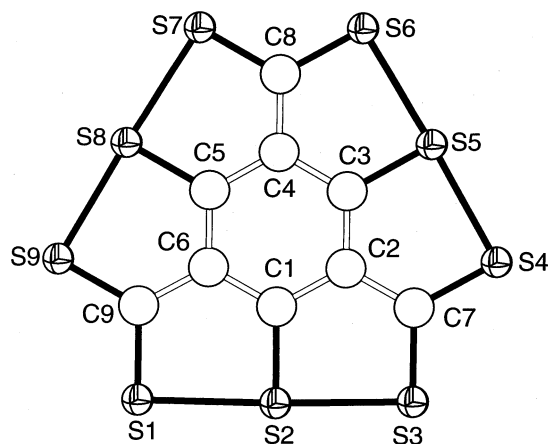
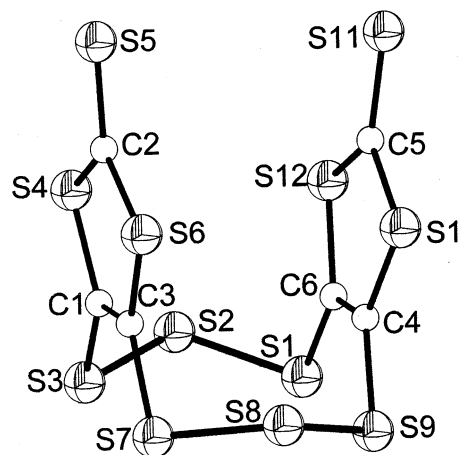
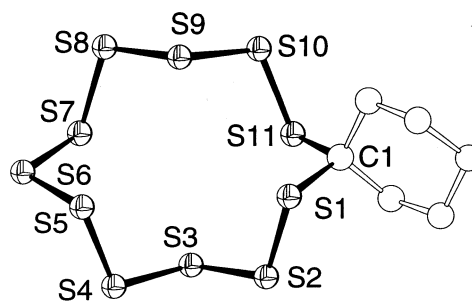
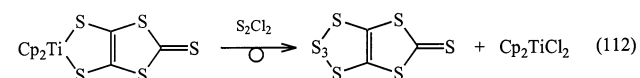
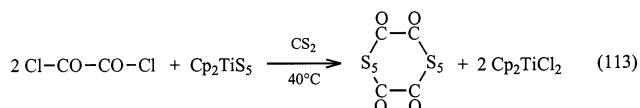


Figure 3. Molecular structures of three cyclic polysulfanes: cyclohexylidene undecasulfane C₆H₁₀S₁₁ (A; hydrogen atoms omitted) and the two tricyclic carbon sulfides C₆S₁₂ (B) and C₉S₉ (C).

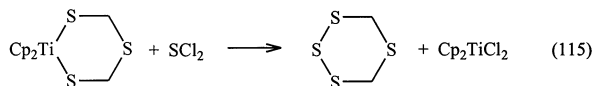
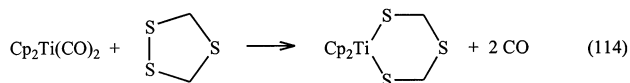
In solution C₃S₈ decomposes to another carbon sulfide, C₆S₁₂, which contains two trisulfane bridges between two 1,3-dithiolane rings, each carrying an additional exocyclic sulfur atom (see below, Figure 3).

Reactions 108–112 are carried out at 0 or 20 °C. At slightly elevated temperatures, Cp₂TiS₅ reacts even with certain C–Cl bonds, as eq 113 shows. The product C₄O₄S₁₀ forms yellow crystals consisting of 14-membered ring molecules (yield 48%):¹⁶³



The use of novel titanocene complexes as precursors for the synthesis of sulfur–carbon heterocycles

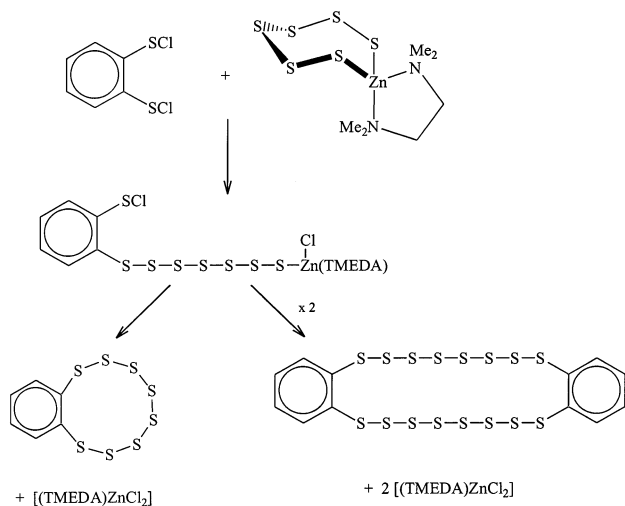
is particularly interesting if the complex is made by insertion of the titanocene unit into an already existing sulfur–sulfur bond using titanocene dicarbonyl as a reagent. The novel complex is then allowed to react with a sulfur chloride. In this way 1,2,4-trithiolane, for example, can be transformed into 1,2,3,5-tetrathiane:¹⁶⁴



In an analogous manner, 1,2,4,6-tetrathiepane has been transformed into 1,2,3,5,7-pentathiocane¹⁶⁴ and lenthionine (1,2,3,5,6-pentathiepane) into 1,2,3,4,6,7-hexathiocane.¹⁶⁵ In principle, these ring enlargement reactions make almost every ring size accessible.

The zinc complex¹⁶⁶ (TMEDA)ZnS₆ **16** has also been used successfully in the preparation of sulfur-rich organic polysulfanes (TMEDA = tetramethylethylenediamine). For example, 1,2-benzene-bis(sulfonyl chloride) on treatment with **16** yields the ten-membered bicycle 1,2,3,4,5,6,7,8-benzooctathiecin **17** (60% yield)⁴⁹ and, under slightly different conditions, the macrocycle (1,2-C₆H₄S₈)₂, which is formally the dimer of **17** (Scheme 2).¹⁶⁷

Scheme 2



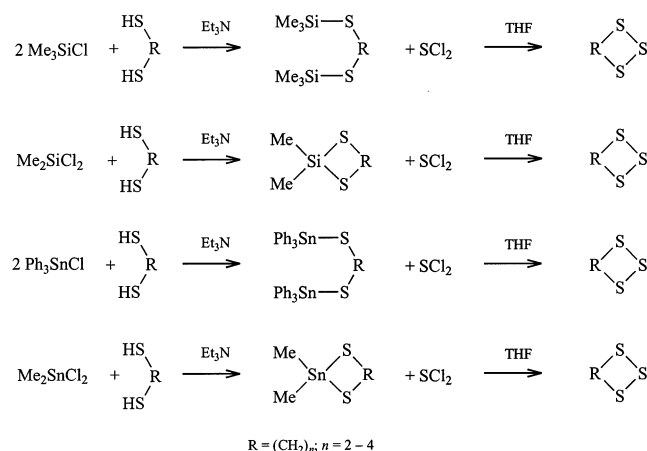
Since similar zinc complexes with differing number of sulfur atoms in the metallacycle are known (depending on the amine used),¹⁶⁸ their reactions with sulfonyl chlorides will probably provide access to more sulfur-rich heterocycles in the future.

9. Cyclic Polysulfanes from Organosilicon or -tin Sulfides and Dichlorosulfanes

As shown in Scheme 3, dithiols (or their anions) react with organosilicon or -tin chlorides to give sulfides which can be cleaved by SCl₂ to synthesize cyclic trisulfanes.¹⁶⁹

The best yields were obtained with (Me₃SiS)₂R and R = C₃H₆ or C₄H₈. In the case of R = C₂H₄, oligomeric compounds were formed. The reaction with SCl₂ is

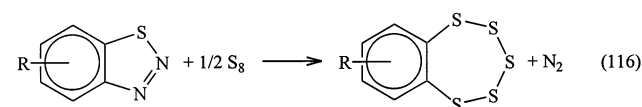
Scheme 3



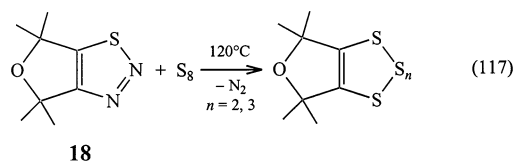
carried out in THF, followed by evaporation of both the solvent and Me₃SiCl. Preparative TLC separation with hexane as an eluent yields a pure product. Cyclic tri- and hexasulfanes were also obtained from Ph₂Sn(μ-S)₂C=CPh₂ by reaction with either SCl₂, SOCl₂ or S₂Cl₂.¹⁷⁰

10. Reaction of Benzothiadiazoles or Related NN Compounds with Elemental Sulfur

1,2,3-Benzothiadiazoles are thermally stable up to 195 °C, but in the presence of elemental sulfur, evolution of nitrogen occurs at 160–170 °C and benzopentathiepins are formed.^{122,171}



With R = H, Cl, CF₃, OMe, NMe₂, or Br, yields of up to 57% have been obtained if some diazabicyclo[2.2.2]octane (Dabco) is added.¹⁷¹ In a similar reaction, the thiadiazole **18**, when heated with elemental sulfur to 120 °C, affords the corresponding cyclic tetra- and pentasulfanes in 18% and 22% yield.¹⁷²

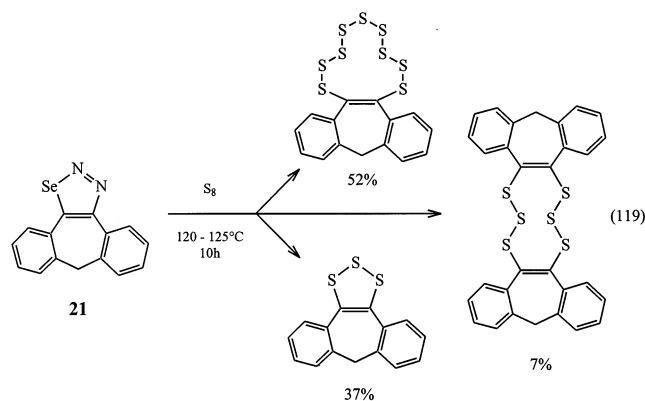
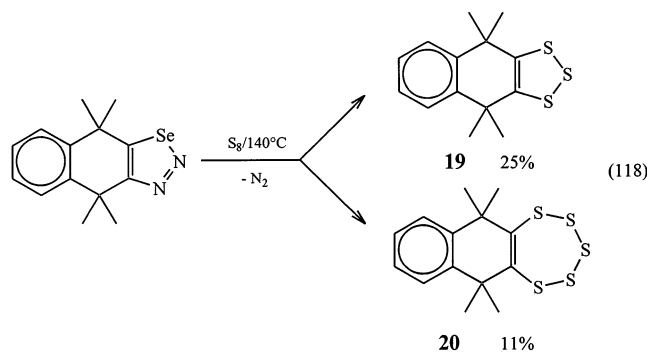


Pyrazolopentathiepins react with a mixture of acetone and ammonium sulfide to form the corresponding tetrathiepins; the ketone fragment (*isopropyl* group) replaces one of the three inner sulfur atoms in a nearly statistical ratio.¹⁷³

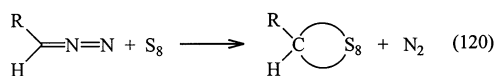
Certain selenadiazoles also react with sulfur to yield cyclic polysulfanes:¹⁷²

On heating or irradiation, **20** is converted to **19** and S₈.¹⁷² When the selenadiazole **21** is heated with sulfur, a complex mixture of sulfurization products was obtained from which the polysulfanes shown in eq 119 were obtained in a pure form by chromatography and crystallization.¹⁷⁴

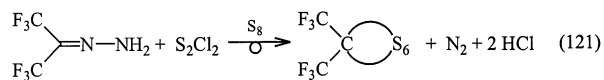
A cyclic octathionane of composition RHCS₈ was obtained in 25% yield on refluxing of S₈ with the



monosubstituted diazomethane RHCN₂ in benzene using the very bulky substituent R = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl.¹⁷⁵



As a solid, this cyclic octasulfane is stable at 20 °C; it survives even in a boiling EtOH/CHCl₃ mixture. Related to reaction 120 is the reaction of hexafluoroacetone hydrazone with S₂Cl₂, which produces the hexathiepane (CF₃)₂CS₆.¹⁷⁵



If the hydrazone is substituted with two bulky groups (R¹ = adamantyl, R² = *tert*-butyl), a tetrathiolane is obtained in the reaction with S₂Cl₂,¹⁷⁶ but with R² = Ph, pentathianes and hexathiepanes are formed in low yield besides thioketones and ketones.¹⁷⁷

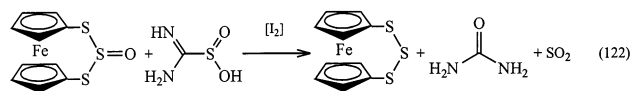
11. Sulfurization of Disulfanes to Polysulfanes

Heating of disulfanes with elemental sulfur in the presence of a polar solvent yields mixtures of sulfur-rich polysulfanes, but these complex mixtures are difficult to separate. Other sulfurization reagents may also be used. For example, 1,2,4,5-tetrathianes react with Na₂S₄ at 0 °C in DMF to the corresponding pentathiepin.¹⁷⁸ To synthesize trisulfanes from disulfanes in high yield, the commercially available sulfur atom transfer reagent Ph₃CSSCl may be used; the reaction according to eq 37 takes place in chloroform at room temperature within ca. 2 h. Dialkyltetrasulfanes were obtained in 71–97% yield from the

corresponding disulfanes by treatment with Ph₃CSSCl as a transfer reagent for S₂ units; see eq 80.

12. Reduction of Sulfane Oxides

Cyclic trisulfane-2-oxides have been reduced to the corresponding trisulfanes by NaI/HClO₄ in THF/H₂O at 20–50 °C.^{131,179,180} Trisulfane 1-oxides, 2-oxides, and 1,1-dioxides may also be reduced to the corresponding trisulfanes by aminoiminosulfonic acid in acetonitrile in the presence of traces of iodine:¹⁸¹



13. Cyclic Polysulfanes from Ketones or Thioketones

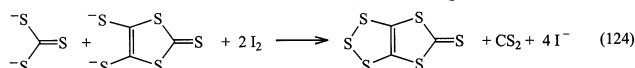
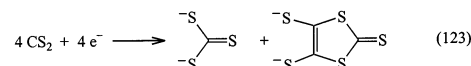
Certain ketones react with H₂S or sodium polysulfide to give cyclic polysulfanes. Formaldehyde and aqueous Na₂S_{2.5} in the presence of chloroform result in 1,2,3,5,6-pentathiepin (lenthionine; see Section VI.B.2).¹²³ Cycloheptanone reacts with ammonium polysulfide at 20 °C to give the tricyclic pentathiepane derivative C₁₄H₂₄S₅ containing a disulfane and a trisulfane bridge between the two cycloalkyl units.¹⁸² Various cyclic and acyclic tri- and tetrasulfanes have been obtained from the corresponding ketones, diketones, or aldehydes and H₂S at temperatures of 30–135 °C and pressures of 50–8500 bar.¹⁰⁷ The use of disulfane H₂S₂ for the transformation of dithiols or dithietanes (“epidissulfanes”) into cyclic tri- and tetrasulfanes in good yield has also been reported.¹⁸³ When 1,2,4,5-tetrathiane is treated with Na₂S₄ in DMF at 20 °C, 1,2,3,5,6-pentathiepin (lenthionine) is formed in 30% yield.¹⁸⁴ Substituted benzothiocarbonates may be converted to benzotrithioles by reaction with NaHS in DMSO.¹⁸⁵

Acetophenone reacts with sulfur in the presence of primary amines to a substituted 1,2,3,4,5,6,7-heptathioan, which forms yellow crystals the structure of which has been determined by X-ray crystallography.¹⁸⁶ Thioketones react with elemental sulfur in the presence of catalytic amounts of PhONa at room temperature to 1,2,4,5-tetrathianes and, with more sulfur, to 1,2,3,5,6-pentathiepanes.¹⁸⁷

14. Miscellaneous Reactions for the Synthesis of Cyclic Polysulfanes

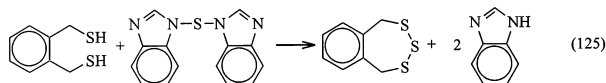
Cyclic tetra-, penta-, and hexasulfanes were obtained from the corresponding di-, tri-, and tetrasulfanes, respectively, by treatment with Ph₃CSSCl as a transfer reagent for an S₂ group; see eq 80.¹¹⁰

Electrochemical reduction of CS₂ in either DMF or MeCN yields the trithiocarbonate together with 4,5-dimercapto-1,3-dithiole-2-thione dianions, which, on oxidation by iodine, give the binary carbon sulfide C₃S₆ in good yield.¹⁸⁸

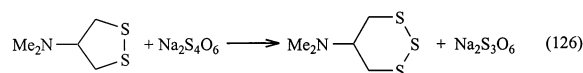


The bicyclic C_3S_6 is a yellow solid which is sparingly soluble in CS_2 .¹⁸⁸

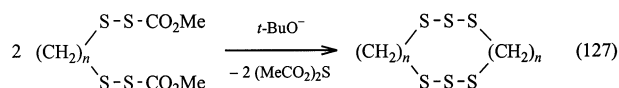
The use of *N,N*-dibenzimidazolyl sulfide for the synthesis of cyclic polysulfanes by reaction with dithiols has been explored. In many cases, oligomers or low-molecular mass polymers are formed. However, α,α' -dimercaptoxylylene yields the benzotrithiepin shown in eq 125 when stirred with the imidazolylsulfide in benzene at 20 °C:¹⁸⁹



4-(*N,N*-Dimethylamino)-1,2-dithiolane is transformed to the corresponding trithiane by reaction with sodium tetrathionate at 20 °C and pH 7.8 (yield 65%):¹⁹⁰



A mixture of S_8 and phosphorus(V)-sulfide may also be used to sulfurize organic compounds: certain cyclic disulfanes are transformed to the corresponding trisulfanes.¹⁹¹ The reaction of SCl_2 with 1,4-diethoxybenzene, catalyzed by Al_2Cl_6 , in CS_2 or $CHCl_3$ yields a bis-tetrasulfane in which two S_4 units bridge the two benzene rings.¹⁹² Acyclic and cyclic trisulfanes may be synthesized from sulfonyl thiocarbonates by nucleophilic displacement. From 1,6-hexanedithiol and $MeO-C(O)-SCl$, the bis(sulfonyl thiocarbonate) shown on the left side of eq 127 was obtained which on treatment with potassium *t*-butoxide in methanol resulted in a macrocyclic bis-trisulfane:¹⁹³



In this reaction the alkoxide ion displaces the $MeOCO$ group, generating an RSS^- anion which attacks the neighboring molecule producing a dimer which is attacked by another alkoxide ion, etc.; finally, ring closure takes place. Similar reactions were observed for $n = 7, 8,$ and 10 , while for $n < 6$, only polymers were obtained.¹⁹³

Substituted thiiranes can be catalytically converted to substituted 1,2,3,4-tetrathianes or 1,2,3-trithiolanes in high yield using the complex $[Ru(salen)(NO)-(H_2O)](SbF_6)$ as a catalyst ($salen = N,N$ -ethylene-bis-salicylidene aminate). These disproportionation reactions proceed at room temperature in nitromethane solution within several hours, and the corresponding olefins are byproducts. Styrene sulfide and propylene sulfide reacted to form the corresponding olefin and the 4-substituted 1,2,3-trithiolane in a 2:1 ratio. The disubstituted thiirane *cis*-stilbene sulfide was converted to *cis*-stilbene and 1,2,3,4-diphenyl-tetrathiane in a 3:1 ratio.¹⁹⁴

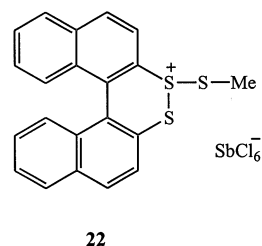
Treatment of nucleophilic heterocycles such as pyrroles and thiophene, and their tetrahydro derivatives, with S_2Cl_2 and a base in chloroform at room temperature provides a simple one-pot synthesis of

heterocyclic fused mono- and bis-pentathiepins. Depending on the base, chlorination of the heterocycle may occur in addition.¹⁹⁵

III. Structures of Organic Polysulfanes

A. General

The stereochemistry of organic sulfur compounds was reviewed very extensively by Laur⁹ in 1972 and that of organic polysulfanes by Rahman et al.¹⁹⁶ in 1970. Since those days, however, enormous progress has been made, especially in the field of sulfur-rich species. The molecular and crystal structures of more than 60 cyclic and acyclic polysulfanes have been determined by X-ray diffraction on single crystals. In rare cases, electron diffraction at the vapor of $R-S_n-R$ molecules has been used to determine the structures. In addition, the structures of several polysulfane oxides such as $R-SO-S-S-R$, $R-S-SO-S-R$, $R-SO_2-S-S-R$, $R-SO_2-S-SO-R$, $R-S-SO-SO-S-R$, and $R-SO_2-S_n-SO_2-R$ ($n = 1, 2$; see Section V.E) as well as of the methylated trisulfane cation $(MeS)_3^+$ ^{197,198} and the chiral sulfonium salt **22**¹⁹⁹ have been determined.



Chain-like organic polysulfanes with up to nine sulfur atoms have been structurally characterized, while in the case of cyclic species, the maximum number of neighboring sulfur atoms was 11, but the total number may be as high as 16. In all cases the S_n backbone was found to be unbranched. It may be characterized by the bond distances d_{SS} , the bond angles α_{SSS} , and the torsional angles τ_{SSSS} ; the latter determine the overall conformation of the molecule. Typical values of these parameters in chain-like $R-S_n-R$ molecules are $d = 205 \pm 4$ pm, $\alpha = 107 \pm 3^\circ$, and $\tau = 85 \pm 20^\circ$. The torsional angles may be positive (clockwise rotation) or negative (counterclockwise rotation). A helical sulfur chain $-S-S_n-S-$ may therefore be a right-handed screw (all τ positive) or a left-handed screw (all τ negative). The order of the signs of τ in such a chain is termed the motif of the chain. Thus, the motif of a helix is either $+++ \dots$ (right-handed helix) or $--- \dots$ (left-handed helix). Less symmetrical S_n chains are obtained if the motif is less regular. In cyclo-octasulfane S_8 , the motif is $+ - + - + - + -$ or $(+ -)_4$; in cyclo- S_6 , it is $(+ -)_3$, and in cyclo- S_{12} , it is $(+ + - -)_3$.¹

Rotation around $S-S$ bonds in acyclic organic disulfanes requires an activation energy of 25–40 kJ mol^{-1} ,²⁰⁰ which is far too low to permit the isolation of the rotational isomers by chromatography, for instance. In the case of $R-S_2-R$, these stereoisomers are mirror images of each other or enantiomers.

Table 4. Geometrical Parameters of Symmetrically Substituted Chain-Like Polysulfanes R-S_n-R (*n* > 2; Bond Lengths *d*, Bond Angles α , and Torsion Angles τ)

R	method ^a	<i>n</i>	<i>d</i> _{ss} (pm)	α _{sss} (deg)	τ _{ss} (deg) ^b	ref
Me	ED	3	204.60	107	80	207a
F ₃ C	ED	3	204.0	105.3	89	28
F ₃ C	X	3	204.1	106.7	88.5	28
ICH ₂ CH ₂ ^c	X	3	205	113	82	207b
2-O ₂ NC ₆ H ₄ ^d	X	3	205.0, 205.4	106.4	81.7, 87.8	209
2-O ₂ NC ₆ H ₄ ^e	X	3	206.0	110.6	79.6	208
Cl ₃ C	X	3	203.4, 203.4	106.0	93, 95	210
CN ^c	X	3	207.1	105.3	87	211
MeCSC(O) ^c	X	3	204.0	107.8	83.1	212
(Me ₃ Si) ₃ C	X	3	205.7, 206.6	112.5	93.2, 104.6	106
<i>n</i> -C ₁₈ H ₃₇	X	3	202.3, 203.0	106.3	72.8, 67.3	214
<i>n</i> -C ₁₈ H ₃₇	X	4	201.8, 206.0	105.3	65.3, 75.9	214
F ₃ C	ED	4	203.4, 205.4	106.8	84, 98	28
CN	X	4	201.7, 206.8(2x)	106.3, 106.7	84.8	213
4-ClC ₆ H ₄	X	4	206.7, 203.6, 202.3	107.4, 108.4	75.5	216
2-benzothiazolyl	X	4	202.7(2x), 207.3	106.4	78.5	216
MeCSC(O) ^c	X	4	203.2, 205.5	106.2	87.3, 78.8	212
Ph ₃ C	X	5	204, 202, 205, 201	109, 106, 111	76–97	47
Ph ₃ C	X	6	202.4–207.0	104.8–108.5	88.7–101.4	47
CN	X	6	203.4–207.4	105.0–106.0	81.2–94.5	105
(CO) ₄ Mn(PPh ₂) ₂ C	X	6	205.4–211.3	106.7, 107.2	56.2–93.8	111
(CH ₂) ₅ NC(S)	X	6	201.1–204.5	106.6–107.4	81.8–96.4	215
CCl ₃	X	7	201.8–205.9	103.6–107.1	79.7–91.1	46
		8				
CN	X	9	204.1–207.8	104.3–106.8	80.2–94.8	104

^a ED, electron diffraction (gas-phase); X, X-ray diffraction on single crystal. ^b In the case of chiral molecules, the torsion angles of the corresponding enantiomers are obtained by changing all signs to the opposite. ^c Due to the symmetry of the molecule, the number of independent molecular parameters is lower than the number of internal coordinates. ^d Triclinic allotrope. ^e Orthorhombic allotrope.

However, in favorable cases these stereoisomers crystallize from solutions as enantiopure single crystals (100% ee, enantiomeric excess); see below. The torsional barriers of organic polysulfanes R-S_n-R, with *n* > 2, have not been accurately determined yet but may be even lower than those for disulfanes. This can be concluded from the results obtained by high-level ab initio MO calculations on the inorganic species H₂S_n (*n* = 2–4); the lowest torsional barrier at the central bond of H₂S₄ is 26 kJ mol⁻¹.²⁰¹ The easy pseudorotation of cyclic S_n molecules such as S₇ also supports a low torsional barrier of cumulated sulfur-sulfur bonds.²⁰² It therefore can be expected that acyclic organic polysulfanes show a rapid rotational isomerization in solution at 20 °C. The conformational properties of trisulfanes R₂S₃ in the liquid and solid states have been studied by Raman spectroscopy;²⁰³ see also Section III.D, Conformational Studies.

Never has any organic polysulfane been observed that has a branched structure of the polysulfur unit. However, species of this type have been studied theoretically. Dimethyldisulfane Me-S-S-Me is by 84 kJ mol⁻¹ more stable than the isomeric thiosulfoxide Me-S(=S)-Me, and the activation energy for the intramolecular isomerization reaction is 340 kJ mol⁻¹;²⁰⁴ see also Section V.A. While numerous ab initio MO studies of dimethyldisulfane have been published, little theoretical work has been done with the more sulfur-rich derivatives, especially at a high level of theory. However, the energy difference between helical hexasulfane H₂S₆ and its branched isomer (HSS)₂S=S has been calculated at the G3X-(MP2) level of theory as only 53 kJ mol⁻¹ (at 0 K).^{205a} The activation energy for the formation of such

species from the helical ground-state species is expected to be higher than the SS-bond dissociation energy.^{205b}

B. Structures of Chain-Like R-S_n-R Molecules

In Table 4 the structural parameters of the S_n backbone of 24 chain-like polysulfanes with *n* > 2 are compiled.^{111,206–217} The only undisturbed free molecules investigated by electron diffraction on vapors are Me₂S₃, (CF₃)₂S₃, and (CF₃)₂S₄. All other data are derived from X-ray diffraction investigations of single crystals. In the latter case, the molecular conformation may be influenced by intermolecular interactions. It should be noted that the parameters cited have widely differing standard deviations (not shown). Many of these molecules are chiral (so-called helical chirality if the point group symmetry is either C_n or D_n with *n* = 1, 2, ...). While normally chiral molecules crystallize in such a manner that the unit cell contains equal amounts of each enantiomer, there are some cases known in which enantiopure crystals have been obtained. For example, diphenyl disulfane crystallized from ethanol in colorless needles which showed a positive or negative Cotton effect, indicating the presence of only one stereoisomer in each crystal.²¹⁸ Similarly, the nonasulfane S₉(CN)₂ crystallized from CS₂/*n*-hexane mixture as enantiopure crystals (space group P₂₁), despite the many conformations this molecule can adopt.¹⁰⁴

Most trisulfanes adopt a trans conformation with a local symmetry of C₂ for the central X-S-S-S-X unit (motif ++ or --). The term trans describes the position of the two substituents X with respect to the plane defined by the three sulfur atoms.

Dicyanotrisulfane is an exception to the rule since this molecule prefers a *cis* conformation in the solid state, which seems to be the result of the weak interaction of the two nitrogen atoms with the central sulfur atom of a neighboring molecule.²¹¹ The motif of $S_3(CN)_2$ is therefore $+ -$ (or $- +$ for the enantiomer which is present in equal amounts in the unit cell). Even with very bulky substituents, the C–S–S–C backbone does not become planar, as has been shown in the case of $R = (Me_3Si)_3C$.¹⁰⁶ The recent electron diffraction measurements on gaseous dimethyltrisulfane at 383 K have been interpreted with a mixture of mainly *trans*- and little *cis*- Me_2S_3 .²⁰⁶ Two crystal-line forms of bis(2-nitrobenzene)trisulfane have been studied by X-ray crystallography. For the triclinic allotrope $d_{SS} = 205.2 \pm 0.2$ pm, $\alpha_{SSS} = 106.4^\circ$, and $\tau = 81.7^\circ/87.8^\circ$ have been measured (site symmetry C_1). The corresponding data for the molecules in the orthorhombic allotrope (site symmetry C_2) are 206.0 pm, 110.6° , and 79.6° , respectively. The differences between these data demonstrate the “softness” of the polysulfane unit with respect to the impact of intermolecular forces.

$(CF_3)_2S_4$ is the only tetrasulfane investigated in the gas-phase; most probably it is of C_1 symmetry (*cis*–*trans*) with the motif $++-$. This result is in agreement with *ab initio* MO calculations,²⁸ which indicate this conformer to be slightly more stable (by 1.2 kJ mol⁻¹) than the *trans*–*trans* conformer. Electron diffraction experiments have shown that the analogous compound Me–O–S–S–O–Me also adopts a *cis*–*trans* conformation in the vapor-phase but a *trans*–*trans* structure in the solid state.²¹⁹ The five solid tetrasulfanes listed in Table 4 all exist in a *trans*–*trans* conformation, with the torsional angles of equal sign for each enantiomer. The same holds for the only acyclic pentasulfane which has so far been studied structurally and which has a helical S_n unit of motif $++++$ (or $----$). Interestingly, however, the four hexasulfanes do not adopt a helical but a more compact conformation with the motifs $++--+$ (or $--++-$) and $++-++$ (or $--+--$), respectively; the motifs given in parentheses apply to the corresponding enantiomeric molecules which are present in equal number in the unit cells.

Only one chain-like heptasulfane and one nonasulfane but no octasulfane has so far been structurally characterized. The heptasulfane $(CCl_3)_2S_7$ adopts a perfect helical conformation. In the unit cell, right-handed and left-handed helices are packed in a parallel manner. In contrast, the nonasulfane $S_9(CN)_2$ which forms a unbranched chain of 13 atoms adopts an almost cyclic conformation with the motif $++--++-$, which is identical to the motif of an S_9 fragment cut from the S_{12} homocycle by removal of three neighboring atoms. The $S_9(CN)_2$ molecule is chiral, but interestingly, the crystals contain only one enantiomer. The fact that this molecule easily crystallizes and even in 100% ee is astonishing since the number of conformations and enantiomers which will be present in the mother liquor must be very high. In principle, at each SS bond the torsion angle may

be positive or negative resulting theoretically in $2^8 = 256$ different molecules of composition $S_9(CN)_2$. Many of these structures will be impossible because of too close contacts between nonbonded atoms. Nevertheless, many conformations of almost equal energy must exist in the solution. The fact that these isomers convert to the two enantiomers found in different crystals of $S_9(CN)_2$ indicates rapid rotational isomerization in solution even at temperatures below 0° C. On melting of $S_9(CN)_2$, these unique conformations in the crystals will return to a mixture of many rotational isomers resulting in a considerable increase in entropy. Therefore, the melting point of $S_9(CN)_2$ is as low as 36 – 38° C (the absolute melting temperature is equal to the quotient from the melting enthalpy and the melting entropy). For similar reasons, the melting point of $(CCl_3)_2S_7$ is also quite low (38° C).⁴⁶

In Figure 2 the molecular conformations of $(Ph_3C)_2S_5$, $(Ph_3C)_2S_6$, $(CCl_3)_2S_7$, and $S_9(CN)_2$ are shown to illustrate the various motifs which to a certain degree must also depend on the polarity and the shape and size of the substituents.

The rotational isomerism which probably exists in solution may be responsible for the fact that so far no single crystals have been obtained for organic polysulfanes with more than nine sulfur atoms in a chain. However, cyclic polysulfanes with up to 11 neighboring sulfur atoms have been structurally elucidated (see below), and the structures of homocyclic sulfur molecules with up to 20 atoms are known.^{220,221}

The molecular parameters in Table 4 show that the SSS bond angles range from 104° to 113° , and the absolute values of the torsional angles at the SS bonds can vary between 65° and 105° .

C. Structures of Cyclic R–S_n–R Molecules

More than 40 cyclic polysulfanes have been investigated by X-ray diffraction on single crystals. These compounds are monocyclic or polycyclic. All ring sizes from 5 to 12 as well as 14, 16, and 20 have been studied, and the number of sulfur atoms in the S_n units varies from 3 to 11 (molecules with less than three sulfur atoms are not subject of this review). This enumeration includes also systems with two independent S_n units ($n = 2$ – 8) in one ring, bridged by carbon atoms. The following are leading references: trisulfanes;^{125,130,162,171,222–224} bis-trisulfane;²²⁵ tetrasulfanes;^{226–228} bis-tetrasulfane;²²⁹ pentasulfanes;^{122,130,142,148,171,230–233} bis-pentasulfane;¹⁶³ hexasulfanes;^{148,233} heptasulfane;⁴⁷ octasulfanes;^{167,175} nonasulfane;¹⁷⁴ undecasulfane.¹⁵⁷

The geometrical parameters of the S_n units in cyclic organic polysulfanes may be quite different from those in chain-like compounds since the ring closure may enforce unusual valence and torsional angles and, as a consequence, the bond distances will be affected. This problem is well-known from the structures of the homocyclic sulfur molecules (cyclo- S_n), which exhibit torsional angles in the range of 0 – 140° ,

bond angles in the range of 101–111°, and bond distances in the range of 200–218 pm.^{220,221}

The conformation of cyclic organic polysulfanes is usually as follows:

(a) Five-membered rings of composition C₂S₃ are envelope-shaped (four atoms SCCS in a plane, one S atom out of plane).^{122,130,171,22,224,234,235} The only known structure of a ring of composition CS₄ is of the same type.²³⁶

(b) Six-membered heterocycles of compositions C₃S₃, C₂S₄, and CS₅ are of chair-conformation like cyclo-S₆ (symmetry D_{3d}).^{125,226,228,232,233,237}

(c) Seven-membered rings of compositions C₂S₅ and CS₆ are of chair conformation like *cyclo*-S₇ (C_s)²³⁸ or distorted (twisted) chairs.^{122,130,142,147,148,171,223,230,231,233,239}

The only investigated asymmetrically substituted hexathiepane ring of type CS₆ is almost of C₂ symmetry.¹⁷⁷

(d) Larger rings either adopt the same conformation as the corresponding sulfur homocycles S₈ (D_{4d}),²⁴⁰ S₉ (C₁),¹⁰⁵ S₁₀ (D₂),²⁴¹ S₁₁ (C₁),²⁴² and S₁₂ (D_{3d})²⁴³ or are of lower symmetry. In the following, only the ring size and ring composition are given:

8: C₄S₄,¹⁶² C₂S₆,²⁴⁴ CS₇^{186,245}

9: CS₈,¹⁷⁵ C₄S₅¹⁴⁸

10: C₄S₆^{162,225}

11: C₂S₉¹⁷⁴

12: CS₁₁¹⁵⁷

> 12: ^{167,229}

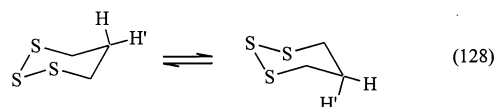
For structures of bicyclic tetrasulfanes, see ref 227. The structures of some carbon polysulfide anions (e.g., C₄S₈²⁻, C₁₆S₁₈⁴⁻) have also been investigated crystallographically.²⁴⁶

The structures of some naturally occurring organic polysulfanes will be described in Section VI.

To illustrate some cyclic structure types, in Figure 3 the results of X-ray structural analyses of C₆H₁₀S₁₁ and of two binary carbon sulfides are shown. The conformation of C₆H₁₀S₁₁ may be derived from the structure of cyclo-S₁₂ by substituting one sulfur atom by the cyclohexylidene group.¹⁵⁷ The binary carbon sulfide C₆S₁₂ is a tricyclic molecule first prepared in 1989.¹⁶² C₉S₉ is formally a thioketone,²⁴⁷ but it contains three linear three-center bonds between adjacent sulfur atoms, resulting in an unusually symmetrical planar system of “two concentric rings” with approximate D_{3h} symmetry. The SS bond lengths of 242 pm are much longer than the single bond distance of 205 pm. The unusual structures and the interesting bonding in compounds of the latter type have been reviewed by Gleiter et al. in 1976.²⁴⁸

D. Conformational Studies

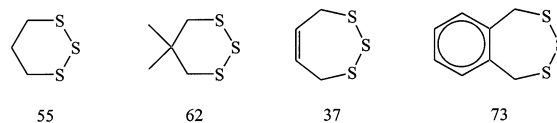
In the case of cyclic polysulfanes, it has repeatedly been observed by ¹H NMR spectroscopy that in solution different conformational isomers exist in equilibrium.^{117,155,249} However, as in the case of acyclic polysulfanes, the energy barriers between these isomers are usually too low to allow a preparative separation at ambient temperatures.¹¹⁷ The barrier for ring inversion reactions as shown in eq 128 has been determined by variable temperature NMR spectroscopy:



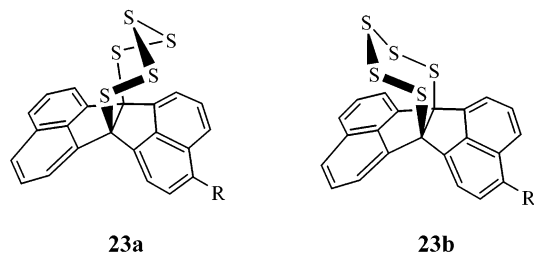
It depends both on the number of sulfur atoms and on the size of the ring as well as on the substituents.

In the case of 1,2,3-trithiane and other cyclic trisulfanes, the following Gibbs activation energies (kJ mol⁻¹) for the ring inversion were derived:²⁴⁹

Scheme 4



For 1,2,3,4,5-pentathiepane (lenthionine **12**), the Arrhenius activation energy of the ring inversion was obtained as 54 kJ mol⁻¹, but in addition, this seven-membered ring undergoes pseudorotation, even at -80 °C.²⁵⁰ A similar energy has been obtained for the ring inversion barrier (boat-to-boat) of a naphtho-1,2,3-trithiocin (ΔH[#] = 64 kJ mol⁻¹).¹¹⁷ However, the sterically crowded acenaphtho-acenaphthylene pentasulfane, containing a pentathiepane ring, does not undergo ring inversion at least up to 100 °C on the NMR time scale, allowing the separate preparation of the two isomers **23a** and **23b** (colorless crystals).¹⁴⁷



The activation parameters for the isomerization of **23a** and **23b** are E_a = 104 and ΔH[#] = 101 kJ mol⁻¹.

For two isomeric pyrazolotetrathiepins containing a trisulfane bridge each, the ring inversion barriers (ΔG[#]) were measured as 75 ± 2 kJ mol⁻¹.¹⁷³ However, for several unsymmetrically substituted benzo-1,2,3,4,5-pentathiepins, chirality was observed, which excludes a rapid chair–chair inversion of the C₂S₅ ring at room temperature.²⁵¹ In fact, the ring inversion barrier of several substituted benzopentathiepins has been determined as ΔG[#] = 100 ± 1 kJ mol⁻¹.²⁵²

Pseudorotation of cyclohexylidene hexasulfane, a CS₆ thiepane, is rapid at room temperature, as was shown by ¹³C NMR spectroscopy.¹⁵⁷ The norbornane derivative C₇H₁₀S₇ containing a nine-membered C₂S₇ ring exists in solution as two conformers, as was shown by ¹H NMR spectroscopy.¹⁵⁵

IV. Analysis of Organic Polysulfanes

A. General

A comprehensive review on the analytical chemistry of organic di- and polysulfanes was published by Cardone in 1972 (340 pages, 1200 references):¹⁰

this review summarizes the physical properties such as density, boiling point, refractive index, vapor pressure, molar refraction, parachor, dipole moment, viscosity, optical rotation, and crystal data as well as the application of several analytical techniques such as thermal analysis, mass spectroscopy, ^1H NMR spectroscopy, IR and Raman spectroscopy, UV-vis spectroscopy, polarography, liquid chromatography, including TLC, paper chromatography, gel permeation, and ion exchange chromatography, partition chromatography, electrophoresis, and gas chromatography. In addition, the chemical treatment of polysulfane mixtures prior to analysis (pyrolysis, reduction to RSH or H_2S , oxidation by bromine, nucleophilic degradation by sulfite, cyanide, or tertiary phosphanes) has been reviewed.¹⁰ More recently the reductive desulfurization of organosulfur compounds by hydrogen-containing nickel boride (Ni_2B) at room temperature has been described which turns C-S bonds into C-H bonds²⁵³ or, if deuterated Ni_2B or Co_2B are used, into C-D bonds.²⁵⁴ The boride reagents are prepared in situ from nickel (cobalt) chloride and sodium tetrahydroborate in methanol-tetrahydrofuran.

The preparation of organic polysulfanes usually results in mixtures of R_2S_n molecules. Even after pure substances have been obtained, these tend to decompose by equilibration with other chain lengths or ring sizes and by formation of elemental sulfur according to eqs 129 and 130:



$$x = 6 - 8$$

These reactions are accelerated by light, heat, and numerous catalysts, of which strong nucleophiles are most effective. In addition, silica gel, alumina, and other porous and finely divided solids catalyze the above reactions. Therefore, conventional liquid chromatography, including paper chromatography, may yield erroneous results. The same holds for gas chromatography since the low vapor pressure of many organic polysulfanes requires high injector and column temperatures. Equally problematic is mass spectrometry if the sample has to be heated to evaporate or if a heated ion source is used. Reliable quantitative data about a mixture of organic polysulfanes can best be obtained by either NMR spectroscopy or by reversed-phase high-pressure liquid chromatography (RP-HPLC).

B. NMR Spectroscopy

In a chain-like compound $\text{R-S}_n\text{-R}$, the chemical shift of the protons of R will depend on the chain length n . This is most obvious from the ^1H NMR spectra of the inorganic sulfanes H_2S_n . All members of this homologous series with n ranging from 1 up to 35 have been identified in this manner.²⁵⁵ In other words, the chemical shift of the chain-terminating hydrogen atoms depends on the chain length. Similar situations can be expected for alkyl substituted sulfanes (methyl, *tert*-butyl, *i*-propyl) which exhibit

simple spectra.²⁵⁶ In the case of aryl substituted or cyclic organic polysulfanes, the spectra may be too complex to analyze these mixtures of homologous compounds quantitatively. In such cases, HPLC analysis is the method of choice. Nevertheless, in favorable cases a clear dependence of the proton shifts on the number of sulfur atoms of homologous molecules has been observed (e.g., dicyclopentadienylpolysulfanes¹²⁰).

C. Chromatography

Reversed-phase HPLC is a particularly gentle separation technique which may be used for qualitative and quantitative analysis of mixtures of R_2S_n molecules as well as for the preparative separation of small amounts of sample. The resolution power of HPLC approaches that of gas chromatography if stationary phases of low particle size (10, 5, or 3 μm) are used. The most widely used stationary phase is the C18 phase, i.e., silica gel covered by $-\text{SiMe}_2-$ ($\text{C}_{18}\text{H}_{37}$) groups which are linked to the surface by the very strong disiloxane bonds (Si-O-Si). This surface modification is produced by reaction of the silanol groups (SiOH) of silica gel with suitable chlorosilanes Cl-SiR_3 .²⁵⁷ The long $\text{C}_{18}\text{H}_{37}$ alkyl chain renders the formerly polar surface of the silica gel totally nonpolar, and if all OH groups have reacted, a chemically very inert but still highly porous material is obtained. The mobile phase then has to be polar, and methanol or mixtures based on methanol are very often applied.²⁵⁸ To increase the polarity of the mobile phase, a few percent of water is added; to decrease the polarity, cyclohexane may be used. The higher the polarity is, the greater the retention time of nonpolar molecules will be.

Sulfanes all have a very strong and broad UV absorption near 220 nm, with a large tail on the longer wavelengths side. Therefore, application of a UV absorbance detector operating at any wavelength of between 220 and 260 nm is recommended. The high extinction coefficients of polysulfanes result in very low detection limits and very dilute samples may therefore be applied which in turn improves the resolution power of the column. In this way, no problems with the sometimes low solubility of sulfur-rich species in the polar mobile phase are to be expected. The total sample concentration may be as low as 0.1 mg L^{-1} using a 10 μL loop injector and a column of 8–10 mm inner diameter.

The main problem with HPLC analysis is, of course, the peak assignment. LC-MS systems are available but are far from being standard equipment. Some help can be expected from a diode-array detector, which allows the on-line measurement of the UV-Vis absorption spectra of the separated sample components during chromatographic separation, e.g., in the range 200–800 nm. Unfortunately, the absorption spectra of organic polysulfanes^{13,29,155,259} are not very specific. The measurement of absorption spectra under static conditions cannot be recommended since polysulfanes rapidly decompose or react with the solvent on UV irradiation.

Peak identification normally requires reference substances to determine the retention time. To make

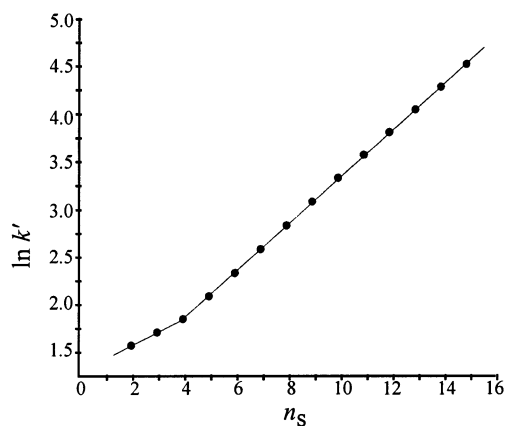


Figure 4. Relationship between the logarithm of the capacity factor K and the number of sulfur atoms in $(C_8H_{17})_2S_n$ molecules.

sure that the retention times of two substances do not agree just by chance, they should be measured at different compositions of the mobile phase. If a homologous series of compounds R_2S_n is to be analyzed, it is of great help that the retention behavior systematically depends on both R and on the number n of sulfur atoms in the ring or chain. For a nonpolar molecule, the retention time t_R will be larger if either R or n is larger than in a reference molecule. Probably it is the surface area of a molecule which determines the retention behavior.^{257,258} In other words, t_R of Et_2S_3 is larger than that of Me_2S_3 , and Me_2S_4 elutes later than Me_2S_3 . Even the small size or surface area difference between isomeric alkyl groups (*n*-butyl, *i*-butyl, *tert*-butyl) results in different retention times. However, if the substituents contain polar groups which increase the solubility in the polar mobile phase, the retention times will be lowered.

In this context the capacity factor $K' = (t_R - t_0)/t_0$ is a very useful quantity. The dead time t_0 of the chromatographic system is roughly the time the eluent needs to travel from the injector to the detector. It may be determined by injection of a methanol/water mixture since H_2O does not show any significant retention in a C18 column. For cyclic^{116,120,155} and acyclic^{22,44,47,258} organic polysulfanes which are members of a homologous series, it has been found that the logarithm of the capacity factor is a linear function of the number of sulfur atoms:

$$\ln K' = a \cdot n + b \quad (131)$$

This relationship was first observed in gas chromatography of dialkylpolysulfanes.⁹⁶ As an example, experimental retention data of di-*n*-octylpolysulfanes $(C_8H_{17})_2S_n$ ⁴⁹ are shown in Figure 4. These linear relationships are extremely helpful since they allow the identification of single members of a homologous series from their retention times by means of inter- and extrapolation. However, sometimes a long series is characterized by two linear relationships of slightly differing slope, one for the first three or four members and another one for the higher members.

The retention times and capacity factors depend, of course, on the chromatographic system and its operating conditions (flow, eluent composition, temperature, column length, particle size, type of sta-

tionary phase, etc.). A more independent measure of the retention properties is provided by the Kovats' retention indices, which are well-known in gas chromatography. This index simply relates the retention time of a substance to the retention time of reference substances measured under identical conditions. The tremendous advantage of the retention index is that it is independent of the chromatographic system and only depends on the eluent composition, the type of stationary phase, and the temperature. Therefore the retention index is a characteristic parameter similar to the chemical shift in NMR spectra, which is also related to the resonance signal of a reference substance.

A number of retention index values of organic polysulfanes have been published.^{44,49,155} They may be calculated as follows.²⁶⁰ The homocyclic sulfur molecules S_6 , S_8 , S_9 , and S_{10} are recommended as reference substances because they are easy to make (see below), have high extinction coefficients in the UV,²⁶¹ and possess retention times similar to those of organic polysulfanes.²⁶² To these molecules the sulfur-based retention index values (*RS* values) of 600 (S_6), 800 (S_8), 900 (S_9), and 1000 (S_{10}) are assigned by definition.²⁶⁰ A plot of $\ln K'$ of these four molecules versus these defined *RS* values gives a straight line according to eq 132:

$$\ln K' = a \cdot RS + b \quad (132)$$

After the parameters a and b have in this way been determined, they are used to derive the *RS* value of the unknown substance. This substance is measured under identical conditions as for the sulfur rings, the capacity factor is calculated from eq 131, and $\ln K'$ is used to calculate the *RS* value of the unknown substance from eq 132. These *RS* data are practically identical when determined from retention data measured with different HPLC systems in different laboratories!

The necessary solution of S_6 , S_8 , S_9 , and S_{10} in CS_2 is prepared as follows: commercial elemental sulfur (1 g) is heated in a test tube to near 200 °C (oil bath) for ca. 2.5 h, cooled slowly to ca. 130 °C (freezing point 115 °C), and poured into liquid nitrogen, resulting in a fine yellow powder which is extracted by CS_2 at 20 °C. The yellow solution contains all sulfur rings from S_6 to S_{20} and is stable at 4 °C in the dark if not too concentrated.^{64,262,263} The peak assignment is straightforward since S_8 gives the tallest peak (besides CS_2 , which comes off the column first). The S_8 peak is preceded by the signals of S_6 and S_7 , and followed by S_9 , S_{10} , etc.²⁶² However, S_7 is not used for the calculation of *RS* values since it does not fit eq 131 very well.

Examples. Chain-like homologous polysulfanes with 2–23 sulfur atoms have been separated by reversed-phase HPLC,²⁶⁴ while cyclic *iso*-propylpolysulfanes Me_2CS_n , with n ranging from 5 to 34, have been separated by the same technique.¹⁹ Furthermore, alkoxythiocarbonylpolysulfanes $[ROC(S)]_2S_n$ (xanthates)²⁶⁵ and alkylthiocarbonylpolysulfanes $[RSC(O)]_2S_n$ as well as alkoxythiocarbonylpolysulfanes⁵⁶ may be analyzed by RP-HPLC. The separation of cyclic methylenesulfanes by RP-HPLC has

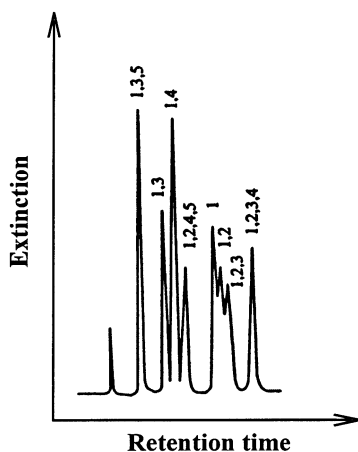


Figure 5. Chromatographic separation of the cyclic methylene sulfides $(\text{CH}_2)_{6-n}\text{S}_n$, with $n = 1, 2$ (three isomers), 3 (two isomers), and 4 (two isomers) by HPLC. The numbers give the positions of the sulfur atoms in the ring (e.g., "1,3" means 1,3-dithiane).

also been reported and the impact of the ring size, number of sulfur atoms, and number of C–S bonds per molecule on the retention time has been elucidated.¹¹⁶ In Figure 5 the HPLC separation of six-membered methylenesulfanes $(\text{CH}_2)_{6-n}\text{S}_n$, with $n = 1-5$, is shown: even the isomeric dithianes 1,2-, 1,3-, and 1,4- $(\text{CH}_2)_2\text{S}_4$ are well separated. Since the retention time is an unambiguous function of the ring size, the number of S atoms, and heteronuclear bonds, the retention of new cyclo-methylenesulfanes can be predicted.¹¹⁶

D. Raman Spectroscopy

Sulfur-rich compounds give very intense Raman spectra since the valence electrons in S–S bonds are highly polarizable. Therefore, Raman spectroscopy has always been a powerful research tool in this area of chemistry, especially after laser Raman spectroscopy was introduced. On the other hand, sulfur-rich compounds are light-sensitive, decomposing by homolytic cleavage of the S–S bonds. Therefore, certain precautions have to be obeyed if one wants to record Raman spectra without any sample decomposition. The wavelength of the laser should be in the red spectral region or in the near-infrared (using a Nd:YAG laser). The red line of a krypton laser can also be recommended. Blue and green lines of argon lasers will unavoidably result in some sample decomposition. This decomposition can be reduced if the sample is cooled to $-100\text{ }^\circ\text{C}$ or below which at the same time results in smaller line widths and in this way improves the spectral resolution.

Numerous Raman spectra of organic polysulfanes have been reported. The S–S stretching vibrations are usually observed in the region $400-500\text{ cm}^{-1}$ and the bending modes show up below 350 cm^{-1} . For a theoretical treatment and literature survey of the vibrations of sulfur chains in R_2S_n molecules with $\text{R} = \text{H}, \text{C}_6\text{H}_5, \text{C}_2\text{H}_5, \text{CCl}_3$ and $n = 4-12$, see ref 266.

E. XANES Spectroscopy

X-ray absorption near edge structure (XANES) spectroscopy is a sensitive probe of the coordination

number and geometry as well as of the effective charge of a chosen atom within a molecule. Recently, there have been a number of XANES studies at the sulfur K-edge demonstrating the sensitivity of the spectra to the local geometric and electronic environment of the sulfur atoms.²⁶⁷⁻²⁶⁹ Structural information deduced from XANES measurements by a fingerprint method is sufficient in many cases for solving analytical problems. This has been demonstrated, for example, in studies on the organosulfur speciation in coal²⁷⁰ and rubber.²⁷¹

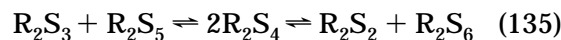
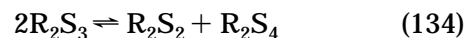
The method involves the irradiation of a sample with polychromatic X-rays (synchrotron radiation), which inter alia promote electrons from the innermost 1s level of the sulfur atom to the lowest unoccupied molecular orbitals. In the present case, these are the C–S and S–S antibonding σ^* -MOs. The intensity of the absorption lines resulting from these electronic excitations are proportional to the number of such bonds in the molecule. Therefore, the spectra of diorganopolysulfanes show significant differences in the positions and/or the relative intensities of the absorption lines if either the number of sulfur atoms or the substituents R are varied.²⁷² Solid, liquid, and gaseous samples can be measured; see also Section VII.B.

V. Reactions of Organic Polysulfanes

Of the many reactions known for polysulfanes, only the following types will be dealt with since they are of general importance for inorganic and organic polysulfur compounds: interconversion, sulfur transfer reactions, replacement reactions, nucleophilic displacement reactions, and oxidation reactions with conservation of chain length. For the discussion of some of these reactions, thermodynamic data are helpful. It seems that the data critically reviewed by Benson² are still the most reliable.

A. Interconversion Reactions

The formal exchange of sulfur atoms between molecules containing S–S bonds is called interconversion; examples are given in eqs 133–135:

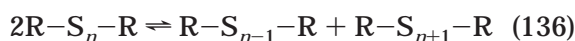


Such reactions are reversible and proceed at moderate temperatures ($0-120\text{ }^\circ\text{C}$) when compounds with cumulated S–S bonds (polysulfanes, elemental sulfur) are considered. The rate of reaction at a certain temperature very much depends on the particular compound and on the solvent. Interconversion reactions are promoted by UV radiation as well as by cationic, anionic, and nucleophilic catalysts (which may be present as impurities!). The reaction mechanisms will, of course, be different in these various cases. A number of reaction types possible under noncatalyzed conditions and with exclusion of light has been critically reviewed in 1982.²²¹ Originally it

had been thought that homolytic bond scission is the first and rate-determining step in all cases. However, dissociation energies of cumulated S-S bonds as in sulfur homocycles and chain-like organic polysulfanes^{1,2} are above 130 kJ mol⁻¹, while some interconversion reactions proceed slowly, even at ambient or slightly elevated temperatures. Therefore, several alternatives for a formal exchange of S atoms or S₂ units between molecules have been proposed.²²¹ These will be discussed below after the equilibrium positions of reactions 133 and 135 have been described in some detail.

If S₈ is dissolved in a polar solvent like methanol or acetonitrile, it equilibrates with S₇ and S₆ even at ambient temperatures.²⁷³ At equilibrium the product distribution is 98.9% (by weight) S₈, 0.77% S₇, and 0.30% S₆ at a total sulfur concentration of 0.12 g L⁻¹. The time needed to establish the equilibrium decreases with the polarity of the solvent (several days in methanol). In the nonpolar solvent carbon disulfide, the equilibrium can be more rapidly established (within hours) by heating to 130–155 °C.²⁷⁴ Under these conditions up to 7 mol % S₇ and 2 mol % S₆ were observed at a total sulfur concentration of 0.3 mmol g⁻¹(solution); the reaction was found to be of first order with an Arrhenius activation energy of 95 kJ mol⁻¹. In highly purified methanol as used for HPLC analysis, the reaction rate is much lower than in commercial solvents even if the producer claims "chromatographic purity".

Equilibrium reactions as shown in eqs 136 have been studied for n = 4–10 and R = n-octyl using HPLC analysis of the product mixture:⁷¹



The following equilibrium constants $K_c = c(n-1) \cdot c(n+1)/c^2(n)$ were derived (mean values for the temperature region 135–155 °C):

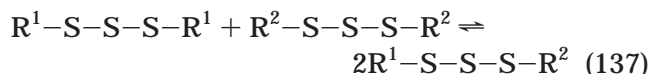
n:	4	5	6	7	8	9	10	>10
K _c :	0.95	0.78	0.72	0.85	0.80	0.96	0.96	1.00

According to these data, the penta-, hexa-, hepta-, and octasulfanes are significantly less stable thermodynamically than the shorter- and longer-chain homologues.

Dimethyltrisulfane, dissolved in benzene, disproportionates at 80 °C very slowly to an approximately 1:1 mixture of di- and tetrasulfane, the equilibrium being reached within 20 days. The use of nitrobenzene as a solvent did not accelerate the reaction significantly. Liquid dimethyltetrasulfane interconverts on heating to 80 °C within 5 h to a mixture of tri-, tetra-, and pentasulfane, together with small concentrations of hexasulfane; only on prolonged heating are small amounts of disulfane formed as well. Addition of azoisobutyronitrile as a radical scavenger suppressed the thermal decomposition of the tetrasulfane at 80 °C almost completely.²⁷⁵

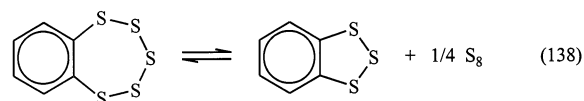
If an equimolar mixture of two dialkyltrisulfanes is heated in benzene to 130–150 °C for several hours (in the presence of diphenyl ether as internal standard), a complete scrambling of the substituents

takes place, and a statistical distribution of products is obtained:



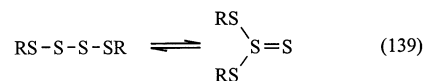
With R¹ = C₂H₅ and R² = n-C₃H₇, the equilibrium constant $K_c = c^2(R^1S_3R^2)/c(R^1_2S_3) \cdot c(R^2_2S_3)$ has been determined as equal to 4. Small amounts of the corresponding di- and tetrasulfanes are formed only after longer heating times. Since tetrasulfane accelerates the ligand exchange of the trisulfanes, the reaction is autocatalytic. Because of this difficulty and because of the reversible nature of these reactions, the reported first-order kinetics and the activation energy of 110 kJ mol⁻¹ for the ligand exchange are doubtful. The authors explained their results by a radical chain reaction mechanism (see below).⁶⁹

A special type of interconversion reaction is the equilibrium between pentathiepanes (or -thiepins) and trithiolanes (or -thioles), which has been observed by several authors and which is schematically shown in eq 138:^{122,139}

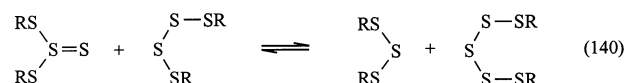


6-(Trifluoromethyl)benzopentathiepin decomposes in methanol solution at room temperature in a first order reaction to the trithiole; eventually a 1:1 mixture of the two species is obtained. No other species than those shown in eq 138 were detected by HPLC and ¹⁹F NMR spectroscopy. No reaction took place in hexane, but addition of diethylamine resulted in the same equilibrium mixture as in methanol. With other substituents on the benzene ring, different ratios of the two heterocycles were observed.¹²²

Possible Reaction Mechanisms. If single sulfur atoms are to be transferred, one might think of a reaction sequence as shown in eqs 139 and 140. The first step is an isomerization of the unbranched sulfane to a thiosulfoxide:



The terminal sulfur atom may then be transferred to a neighboring molecule:



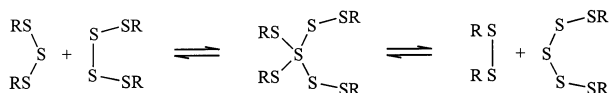
However, from ab initio MO calculations, it is known that isomerization of an unbranched sulfur chain to form a branched structure is fairly endothermic, and a substantial activation energy is needed in addition. This follows from the experiences with smaller model compounds. Intramolecular isomerization of dimethyldisulfane to the thiosulfoxide requires an activation energy of 340 kJ mol⁻¹, which is higher than the C-S bond dissociation energy.²⁰⁴

Similarly, the activation energy needed to isomerize dichlorodisulfane Cl-S-S-Cl to the thiothionyl chloride $\text{Cl}_2\text{S}=\text{S}$ has been calculated at a high theoretical level as 214 kJ mol^{-1} .²⁷⁶ This result for the dichlorodisulfane is particularly interesting since this molecule can serve as a model compound for a section of a sulfur chain-like $-\text{S-S-S-S}-$ with which it is isoelectronic. In the case of hexasulfane H_2S_6 , the symmetrical thiosulfoxide H-S-S-S(=S)-S-S-H is only 53 kJ mol^{-1} less stable than the helical isomer [at the G3X(MP2) level of theory], but the activation energy for its formation is unknown.^{205a} The thiosulfoxide isomer of pentathiepin $\text{H}_2\text{C}_2\text{S}_5$ (C_1 symmetry) is over 67 kJ mol^{-1} less stable than the unbranched heterocycle in its chairlike ground state (C_3), but the formation of the thiosulfoxide (via a twisted ring intermediate) requires an activation energy of more than 224 kJ mol^{-1} (at the B3LYP/6-31G* level) in the gas phase,^{205b} which is more than the SS bond dissociation energy of 150 kJ mol^{-1} !

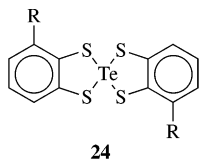
Under these circumstances reactions as shown in eqs 139 and 140 are highly unlikely. The same holds for the formation of S_2 from thiosulfoxides. Simple thiosulfoxide derivatives of the type X-S(=S)-X are stable at ambient temperatures only with $\text{X} = \text{F}$ ²⁷⁷ and OR ²⁷⁸ (in the latter case, an additional "ring effect" is needed, i.e., the two OR groups are part of a ring).

Another plausible pathway which has been proposed for interconversion reactions involves a σ -sulfurane type intermediate or transition state; see Scheme 5.²²¹

Scheme 5



Sulfuranes SX_4 are known in large numbers with $\text{X} = \text{F}, \text{Cl}, \text{OR}, \text{R}$ (= organyl), and others.²⁷⁹ Although tetrahasulfuranes $(\text{RS})_4\text{S}$ have never been observed, the tetrathiatellurane **24** ($\text{R} = \text{tert}$ -butyldimethylsilyl; orange needles, mp 188°C) has been prepared from TeCl_4 (83% yield).²⁸⁰

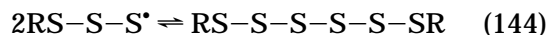
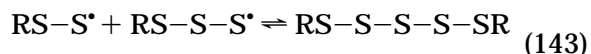
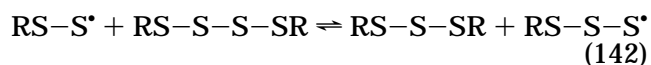


If the hypervalent species formed in Scheme 5 undergoes a Berry pseudorotation process, certain axial and equatorial substituents will exchange their positions. The subsequent elimination of di- and pentasulfane by ligand-coupling will then result in a formal exchange of one sulfur atom.

The thermodynamics of the formation of the tetrahasulfuranes $(\text{HS})_4\text{S}$ (from H_2S_2 and H_2S_3) and $(\text{MeS})_4\text{S}$ (from Me_2S_2 and Me_2S_3) has recently been studied by high-level ab initio MO calculations.⁹³ It turned out that the reaction enthalpies (and even more so the activation energies) are higher than the S-S bond dissociation enthalpy of the corresponding

trisulfane. Consequently, homolytic dissociation will occur first. Therefore, the sulfuranes cannot be regarded as thermodynamically favorable model intermediates for the interconversion reactions of polysulfanes or sulfur rings. In other words, the exact mechanism of the low-temperature interconversion reactions is still unknown. But most probably, many of the observed reactions are triggered by traces of nucleophiles present as impurities in the solvents or as functional groups on the surface of the glass bottles used in laboratory experiments; see Section V.D.

Uncatalyzed interconversion reactions at higher temperatures ($>100^\circ\text{C}$) usually proceed via a radical chain reaction mechanism,²²¹ as illustrated by eqs 141–144:



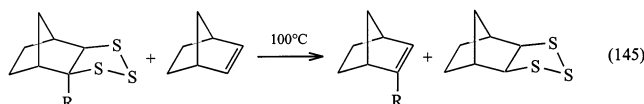
In these reactions only the weakest bonds will break: in tetrasulfanes these are usually the central S-S bonds and only seldomly the CS bonds since the radicals RS-S^* are stabilized by a three-electron π bond which is not present in thiyl radicals R-S^* . Therefore, the polysulfanes with more than three sulfur atoms in the chain do not form thiyl radicals on heating. However, in triphenylmethyl polysulfanes the C-S bond seems to be the weakest in the molecule which dissociates first on heating; see eqs 80 and 105.

Light-induced interconversion reactions also proceed by a radical chain reaction: laser flash photolysis at 308 nm of $t\text{-Bu}_2\text{S}_4$ in cyclopentane solution produced the perthiyl radicals RSS^* , which are characterized by a strong absorption at 368 nm and a weak band near 550 nm. Photolysis of frozen solutions of $t\text{-Bu}_2\text{S}_4$ in toluene at -160°C produced an anisotropic ESR spectrum assigned to RSS^* radicals.²⁸¹ The formation of radicals upon irradiation of solid elemental sulfur at temperatures of 2–70 K with radiation of wavelengths below 430 nm has also been demonstrated by ESR spectroscopy.¹³⁶ In aqueous solution, perthiyl radicals have been produced (besides thiyl radicals RS^*) by photolysis (mercury lamp) of the trisulfanes of penicillamine or cysteine.²⁸² These radicals are also formed in the presence of molecular oxygen, but in this case, sulfate is produced in addition, which originates from the reaction of perthiyl radicals with two equivalents of O_2 .

B. Sulfur Transfer Reactions

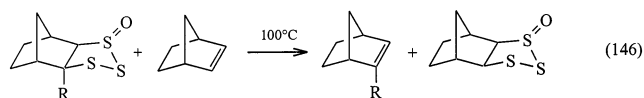
Certain organic di- and polysulfanes on heating seemingly split off S_2 , which may then add to a substrate to form another disulfane.¹⁴⁹ Only recently have transfer reactions for the S_3 and even the S_3O unit been observed.²⁸³ When a substituted (labeled) norbornanetrissulfane is heated with norbornene in

benzene to 100 °C, a clean transfer of the S₃ unit is observed for R = phenyl:



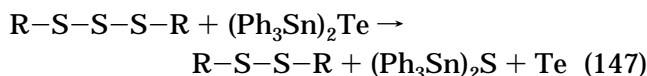
The rate and the yield of reaction 145 depend on the nature of the residue R and of the alkene to which the S₃ unit is to be transferred. If the accepting norbornene is also substituted in the 2-position, the yields differ very much, depending on the substituents: phenyl results in high, methyl in low, and methoxycarbonyl in intermediate yields. If an unsymmetrically substituted norbornadiene is used as an acceptor molecule, the two double bonds react with the same rate to give equal amounts of the two trithiolanes. Most probably, the transfer reaction proceeds by a concerted bimolecular mechanism without free S₂ or S₃ molecules as intermediates.

Norbornanetrithiane may be oxidized by *m*-CPBA (3-chloroperoxybenzoic acid) to give the two isomeric compounds trisulfane 1-oxide and 2-oxide.²⁸³ The 2-oxide may also be prepared from norbornanedithiol and thionyl chloride. Heating the substituted 1-oxide in benzene with norbornene for 12 h to 100 °C resulted in a 50% S₃O transfer.²⁸³



For other thermally induced sulfur transfer reactions, see Section II.B.6.

A special type of sulfur atom transfer occurs when dialkyl- or diaryltrisulfanes are treated with bis(triphenylstannyl)telluride:²⁸⁴



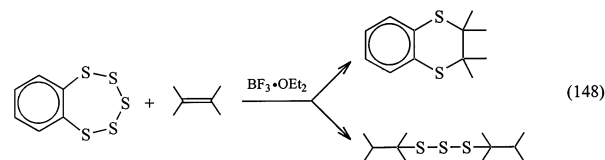
The yields depend on the substituents R and may reach 85%.

C. Replacement Reactions

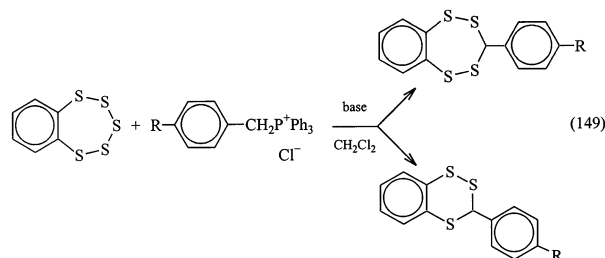
Replacement reactions are defined as reactions resulting in a substitution of parts of the polysulfur unit in a heterocycle by other atoms without any change in ring size. For example, pyrazolopentathiepins react with a mixture of acetone and ammonium sulfide to form the corresponding tetrathiepins; the ketone fragment (*i*-propyl group) replaces one of the three inner sulfur atoms in a nearly statistical ratio;^{122,171} see also Section II.B.6.

Functionalized organic compounds may react with a chain of sulfur atoms by replacement. For example, 1,2-benzopentathiepin C₆H₄S₅ reacts with olefins such as cyclohexene, cyclopentene, butene, or hexene when treated with BF₃·OEt₂ at 20–40 °C. The olefin replaces two sulfur atoms by the two carbon atoms of the former double bond. In the case of tetramethylethene, however, three sulfur atoms were replaced, and the eliminated S₃ fragment added to two mol-

ecules of olefin surprisingly, resulting in bis(1,1,2-trimethylpropyl)trisulfane:²⁸⁵

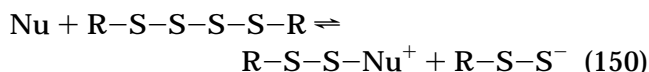


Benzopentathiepins react with phosphorus ylides to form a mixture of benzotetrathiepins and benzotriithiins. The carbanion fragment of the phosphorus ylides replaces one or two sulfur atoms in benzopentathiepin.²⁸⁶

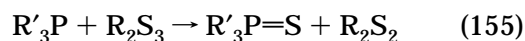
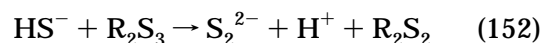


D. Nucleophilic Displacement Reactions at the Sulfur–Sulfur Bond

These reactions are among the most important ones in the chemistry of polysulfur compounds. A strong nucleophile (Nu) may open an S–S bond heterolytically, as shown in eq 150:



In this reaction the anion RSS[−] has been displaced. The relative strengths of various nucleophiles which determine the position of the equilibrium (150) may be given by their thiophilicity. This area of sulfur chemistry has been pioneered by Foss and expertly reviewed by Davis.²⁸⁷ The following species are very strong thiophiles which are able to open any sulfur–sulfur single bond in a polysulfane in a reaction of the type shown in eq 150: thiolates RS[−] and perthiolates RSS[−], hydrogen sulfide HS[−], polysulfides S_{*n*}^{2−} (n = 1, 2, ...), sulfite anions SO₃^{2−}, cyanide ions CN[−], phosphanes R₃P (R = alkyl, aryl, alkoxy, dialkylamino, etc.). The corresponding reactions are depicted in eqs 151–155:

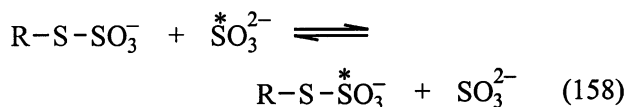
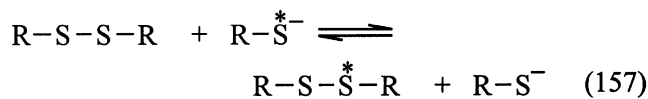


As can be seen, some reagents desulfurize the original polysulfane to the level of disulfanes but some give even monosulfanes R₂S. In the case of R₃P, it depends on R' whether di- or monosulfanes are formed from trisulfanes (see below). Such reactions

display a second-order kinetics. The rate very much depends on the steric requirements and on the "strain" of the S–S bonds to be broken. For example, methanesulfonyl thiocyanate reacts with cyanide according to eq 156:

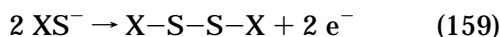


However, *t*-butanesulfonyl thiocyanate does not react with cyanide. Similar observations have been made with reactions 157 and 158, which have been studied using labeled sulfur atoms:

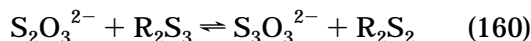


In reaction 158 the relative rates are orders of magnitude smaller with R = *tert*-butyl compared to R = Me. Strained ring systems react much faster with thiolates than comparable chain-like compounds. For example, 1,2-dithiolane reacts about 5000 times faster with *n*-butanethiolate than does di(*n*-butyl)disulfane. The thiophilicity of thiolate ions (RS[−]) very much depends on R: 2,4-dinitrobenzenethiolate is much less thiophilic than benzenethiolate, which in turn is less thiophilic than ethanethiolate.²⁸⁷ In unsymmetrical disulfanes RSSR', the less basic RS[−] group is displaced by an incoming nucleophile like cyanide, sulfite, or thiolate.²⁸⁷ Too weak to open an ordinary S–S bond are the nucleophiles R₃N, OH[−], S₂O₃^{2−}, and SCN[−].

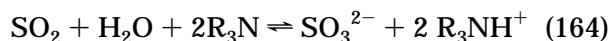
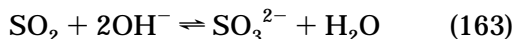
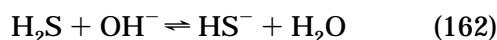
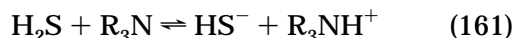
These reactivities can be explained by the oxidative dimerization potential E_0 , derived for eq 159 and the base strength of the nucleophile:



According to a rule by Foss,²⁸⁷ the anions of more positive E_0 will displace anions of lower E_0 . Aqueous thiosulfate is not able to open S–S bonds; therefore, the equilibrium shown in eq 160 is completely to the left:²⁸⁷

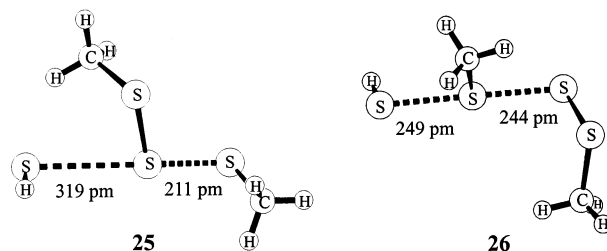


The situation with OH[−] and R₃N is similar. Both nucleophiles are too weak as thiophiles to open an S–S bond. However, sulfur chemists know that alkali hydroxides and amines tend to decompose polysulfur compounds very effectively. This is probably due to secondary reactions of these nucleophiles with ubiquitous traces of either H₂S or SO₂, resulting in the formation of the strong thiophiles HS[−] or SO₃^{2−}.²⁸⁷

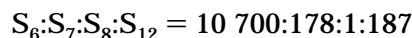


Sulfide and polysulfide ions are very strong thiophiles and displace thiolate from aryldisulfanes. The reaction of sodium sulfide with S₈ in methanolic sodium hydroxide is fast even at −78 °C.²⁸⁷

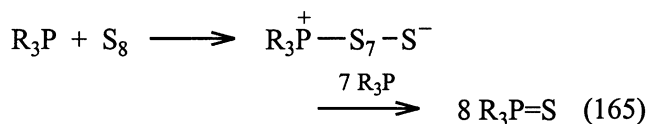
The molecular mechanism of the attack of HS[−] ions on dimethyltrisulfane in the gas-phase has been studied by ab initio MO calculations.^{288a} The reactions proceed by an addition–elimination mechanism. In the transition states **25** and **26**, the incoming sulfur atom of the HS[−] ion forms an almost linear arrangement with two neighboring sulfur atoms of the trisulfane, regardless of whether the central or a terminal S atom is attacked. Electron density from the anion is then transferred into the antibonding σ^* -MO of the attacked S–S bond, which subsequently breaks with formation of either MeS[−] and HSSSMe (attack on central S) or MeSS[−] and MeSSH (attack on terminal S). Attack at one of the terminal sulfur atoms of the trisulfane is kinetically and thermodynamically favored; this reaction proceeds practically without any overall energy change and without any barrier.



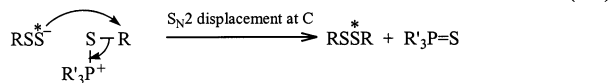
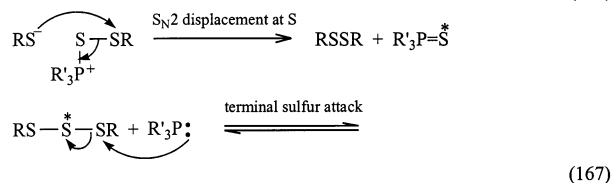
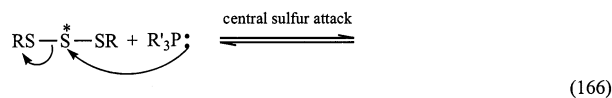
The reactions of tertiary phosphanes with elemental sulfur have been studied kinetically in detail.¹⁵ While trialkylphosphanes and, even more so, trialkoxyphosphanes react with great vigor, certain arylphosphanes react slowly enough for kinetic data to be measured. It was found that diphenyl(2-tolyl)phosphane reacts with homocyclic sulfur molecules S_{*n*} (*n* = 6, 7, 8, 12) in CS₂ at −12 to +35 °C in a second-order reaction to give R₂R'P=S. The activation energies (in kJ mol^{−1}) are 51 (S₆), 40 (S₇), 69 (S₈), and 46 (S₁₂). At 20 °C the relative reactivities (rates) are as follows (S₈ = 1):



Similar dramatic differences are to be expected for cyclic and linear polysulfanes as a function of ring size and inductive as well as steric effects of the substituents. In the case of cyclic species, the first and rate determining step will always be the opening of the ring, resulting in a highly reactive zwitterion which is then rapidly degraded by additional phosphane molecules:²⁸⁷

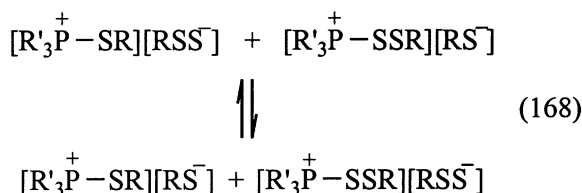


Evidently, the polarity of the solvent will also be of great importance for the stabilization of ionic and zwitterionic intermediates. Reaction rates in water and in aliphatic alcohols have also been studied.²⁸⁹ The desulfurization of di- and trisulfanes by a variety of tertiary phosphanes has been studied repeatedly. In the case of trisulfanes, the initial step may be an attack of the phosphane on either the central sulfur atom or on one of the terminal S atoms, as shown in eqs 166 and 167.²⁹⁰ In both cases a pair of ions is formed:



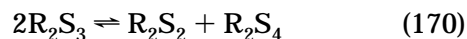
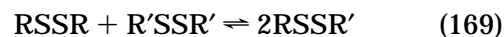
The subsequent steps of these reactions are irreversible. The anions induce a nucleophilic displacement at the cations as follows: in eq 166 the RS⁻ ion attacks the terminal sulfur with formation of R₂S₂, while in eq 167 the RSS⁻ ion attacks the carbon atom linked to the terminal sulfur. In the first case, the central sulfur atom is eliminated, while in the second case, one of the terminal S atoms is eliminated. Radiochemical experiments with trisulfanes containing the central S atom labeled by ³⁵S showed that desulfurization of dialkyltrisulfanes by triarylphosphanes results in 91–99% central sulfur removal, essentially independent of solvent polarity (Et₂O or MeCN), reaction temperature (0–50 °C) type of trisulfane (dibenzyl or dipropyl), and para substituents on Ar₃P. In sharp contrast to this, desulfurization of dialkyltrisulfanes by tris(dialkylamino)phosphanes results in preferential removal of a terminal sulfur atom if the reaction is carried out in Et₂O, while in MeCN more than the statistical amount (33%) of central sulfur is removed. When sterically hindered trisulfanes are used, the rate of desulfurization decreases, and the percentage of central sulfur atom removal increases, as expected.²⁹⁰

Initially, a phosphane attacks a trisulfane both at the central and the terminal sulfur atoms, and there is evidence that the two resulting phosphonium salts shown in eqs 166 and 167 exchange their anions:



The ion pairs on the right side of eq 168 may dissociate into R₂S₂, R₂S₄, and R₃P, and in fact the formation of tetrasulfane was observed. In other

words, tertiary phosphanes (including Ph₃P) like other strong nucleophiles catalyze the exchange and interconversion reactions shown in eqs 169 and 170²⁹⁰



It depends on the phosphane and the solvent which of the reactions 166 and 167 prevails and whether the final product will be a di- or a monosulfane. The latter are usually obtained using (R₂N)₃P, but only in the case of dialkylsulfanes.²⁹⁰ However, if the substituents of the polysulfane are very bulky and consequently hindering the access of the phosphane, different products may be obtained. The cyclic octasulfane mentioned in eq 120 gave the corresponding pentathiane (yield 64%) on treatment with three equivalents of Ph₃P at –78 °C in THF. Refluxing of the mixture with 7 equiv of the phosphane resulted in desulfurization to a thiobenzaldehyde.²⁹¹

The desulfurization of aromatic trisulfanes by triphenylphosphane according to reaction 155 is accelerated by electron withdrawing groups (e.g., NO₂) in the para position of the two aromatic rings, while electron donating groups (e.g., NH₂) in these positions increase the activation energy and therefore decrease the reaction rate.¹⁵

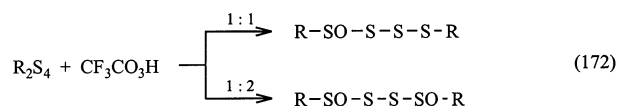
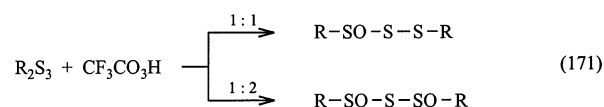
For desulfurization of organic tri- and tetrasulfanes by triorganophosphanes in water or in aliphatic alcohols, see ref 289.

More examples for nucleophilic displacement reactions can be found in Section II, e.g., reactions 2, 6–8, 18, 29–32, 61, 63, 64, 68, 85–87, and 90–94.

E. Oxidation of Polysulfanes to Sulfane Oxides

Sulfane oxides are compounds of the type R₂S_nO_m (n > 1, m = 1, 2, 3, ...) with the oxygen atoms present as sulfoxide or sulfone groups. Disulfane 1-oxides R–S(O)–S–R are also known as thiosulfinates and the 1,1-dioxides are usually termed thiosulfonates. For a rational nomenclature of organic S–O compounds of this type, see Table 2; for a review on oxidized sulfur chains and rings, see ref 292. The oxides of trisulfanes have been expertly reviewed in 1998 by Clennan and Stensaaas.³ In this section the oxides of composition R₂S_nO_m (n > 2) will be briefly reviewed.

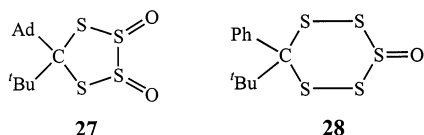
Trisulfane 1-oxides and 1,3-dioxides as well as tetrasulfane 1-oxides and 1,4-dioxides have been obtained by stepwise oxidation of the corresponding sulfanes by peroxy acids (eqs 171 and 172).^{102,124,128,181,293–298}



Dimethyldioxirane (DMD) and ozone (at –78 °C)²⁸³ may also be used as oxidants to prepare sulfoxides,

while *N*-bromosuccinimide was used to prepare sulfones.²⁹⁴ Reactions of this type are of general importance in connection with the oxidative aging of rubber vulcanized by sulfur since such a polymer contains di- and trisulfane groups; see Section VII.B. Using DMD and trifluoromethylmethyldioxirane, bis(*p*-methoxyphenyl)trisulfane has been oxidized to the 1-oxide, the 2-oxide, and the 1,1-dioxide.²⁹⁹

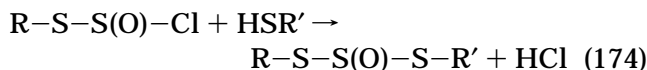
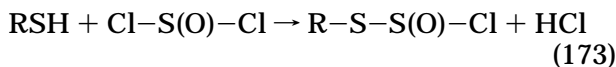
If rather bulky substituents are used, cyclic polysulfanes can be oxidized to sulfoxides in which the SO group is not neighboring to the carbon atom(s). For example, 1-adamantyl-*tert*-butyl-tetrathiolane, when treated with an excess of DMD at $-20\text{ }^{\circ}\text{C}$, gave the tetrathiolane-2,3-dioxide **27**, the structure of which was determined by X-ray crystallography. This disulfoxide decomposes in solution at temperatures above $-10\text{ }^{\circ}\text{C}$, probably with formation of S_2O as a reactive intermediate which has been trapped by reaction with 2,3-dimethyl-1,3-butadiene.³⁰⁰



Oxidation of 6,6-*tert*-butyl phenyl pentathiane by trifluoromethyl peroxy acetic acid at $-20\text{ }^{\circ}\text{C}$ provided the corresponding 3-oxide **28** (yield 41%).³⁰¹

The crystal and molecular structures of a disulfane 1-oxide ($\text{R} = 4\text{-tolyl}$)³⁰² and of several acyclic trisulfane 1-oxides, 2-oxides, 1,1-dioxides, 1,1,3-trioxides, and 1,1,3,3-tetroxides have been determined by X-ray diffraction on single crystals.^{89,283,298,302,303}

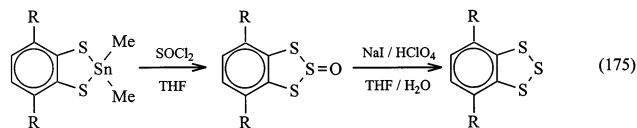
Trisulfane 2-oxides are usually obtained from thionyl chloride and thiols in diethyl ether or in the presence of stoichiometric amounts of pyridine (eqs 173 and 174).^{86–88,304} If 1,2-dithiols or dithiolate metal complexes are used, cyclic trisulfane 2-oxides result, and several of them have been structurally characterized by X-ray crystallography.^{179,252,304} Oxidation of cyclic trisulfanes by peroxy acids sometimes gives mixtures of 1- and 2-monoxides.²⁵² Unsymmetrically substituted trisulfane 2-oxides $\text{RS-SO-SR}'$ are accessible by a stepwise condensation of SOCl_2 with first RSH and then $\text{R}'\text{SH}$; in the case of $\text{R} = 2\text{-naphthyl}$, the intermediate RS-S(O)-Cl has been isolated as a yellow solid. RSS(O)Cl reacts at $0\text{ }^{\circ}\text{C}$ in diethyl ether with thiols to give $\text{RS-S(O)-SR}'$.⁸⁸



The structure of the S_3O group of trisulfane 2-oxides is analogous to the geometrical structure of thionyl chloride SOCl_2 (symmetry C_s). The S-S bond distances are considerably longer (ca. 213 pm)^{89,302} than those in trisulfanes (ca. 204 pm). Ab initio MO calculations on several isomers and conformers of $\text{Me}_2\text{S}_3\text{O}$ showed the 1-oxide to be more stable by 11 kJ mol^{-1} than the 2-oxide. In the case of $\text{Me}_2\text{S}_3\text{O}_2$, the 1,3-dioxide is more stable by 21 kJ mol^{-1} than

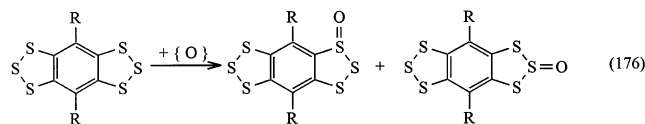
the 1,2-dioxide, but most probably the 1,1-dioxide (sulfone) is the global minimum.³⁰⁵

Benzotrithiole-2-oxides have been obtained from the dimethyltin complex of the corresponding benzo-1,2-dithiol and thionyl chloride.²³⁵



Reduction of the 2-oxide by NaI/HClO_4 provided the trithiole; this trisulfane has been oxidized by NOPF_6 to the trithiolium radical cation, which was studied by ESR spectroscopy. Dissolution of the salt in water provided a mixture of the trithiole-1-oxide and the corresponding 2-oxide. A similar mixture was obtained when the trithiole was dissolved in concentrated sulfuric acid and then hydrolyzed.²³⁵

A most remarkable photochemical isomerization was observed by Sato et al.²⁹⁶ Oxidation of the benzo-bis(trithiole) shown in eq 176 by *m*-chloroperoxybenzoic acid yielded a mixture of the trithiole-1-oxide and 2-oxide ($\text{R} = \text{methyl or ethyl}$):

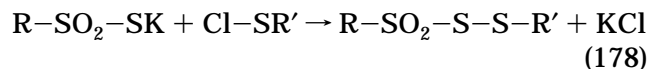


Irradiation of the pure 2-oxide by a mercury high-pressure lamp in acetonitrile resulted in an oxygen migration to the neighboring sulfur atom, thus providing the 1-oxide quantitatively. Other cyclic aromatic trisulfane-2-oxides also showed this intramolecular isomerization, but cyclic nonaromatic derivatives did not. Therefore, it was concluded that irradiation first generates an excited state which rearranges accordingly.

Oxidation of organic polysulfanes by an excess of peroxy acid eventually results in sulfones and disulfones (polysulfane tetroxides):^{102,181}



Polysulfane 1,1-dioxides (sulfones) may also be prepared by reaction of organylthiosulfates with sulfonyl chlorides.³⁰⁶



The molecular structures of several polysulfane tetroxides $\text{R-SO}_2\text{-S}_n\text{-SO}_2\text{-R}$ ($n = 1-3$) have been elucidated by X-ray diffraction on single crystals.^{307–309} The S-S bonds between the sulfone groups and the neighboring sulfane sulfur atoms are longer and therefore weaker (210–214 pm) than ordinary S-S single bonds (205 pm).¹

VI. Natural Occurrence of Organic Polysulfanes

A. General

It is well-known that disulfane-containing compounds, such as proteins, hormones, lipoic acid,

Table 5. Naturally Occurring Chain-Like Diorganopolysulfanes R¹-S_n-R²

R ¹	R ²	n	source	ref
Me	Me	3, 4	shiitake mushroom	316
Me	Me	3	oil made from <i>Ferula asafoetida</i>	317
Me	Me	3	geotrichum candidum	323
Me	2-Bu	3	oil made from <i>Ferula asafoetida</i>	317
Me, Et, Pr	Me, Et, Pr	3	durian fruit	324
HOC ₂ H ₄	HOC ₂ H ₄	3	bacillus stearothermophilus	325
Pr	Pr	3, 4	azadirachta indica	324
2-Bu	2-Bu	3, 4	oil made from <i>Ferula asafoetida</i>	317
Ph-CH ₂	C ₂ H ₄ -OH	3	roots of <i>Petiveria alliaceae</i>	321
Allyl	Allyl	3-6	garlic oil	318, 327
Allyl	Allyl	2-4	adenocalymma alliaceae	315, 343
Alanyl	Alanyl	3, 4	wool hydrolysate	319
3-Oxoundecyl	same as R ¹	3, 4	<i>Dictyopteris plagiogramma</i> (alga)	320
Me	Complex structure	3	<i>Micromonospora echinospora</i> (calichecin)	335
Me	Complex structure	3	<i>Actinomadura verrucospora</i> (esperamicins)	336

enzymes, and other products, occur naturally, and many studies on their biochemical role have been published.³¹⁰ Protein folding influenced by the -S-S- bridges of cystine has been studied intensively, and it is generally accepted now that introducing disulfane bonds into proteins thermally stabilizes the folded state. However, it has been shown that tri-, tetra-, penta-, and even hexasulfanes also occur in organisms or materials produced from them. Such sulfur-rich, low molecular weight natural products are of interest because of their intriguing structures, pronounced flavors, and physiological activity. In Section VI.B, a brief overview will be presented of chain-like and cyclic organic polysulfanes, which have so far been isolated from or detected in biological materials. Extensive reviews on organic sulfur compounds from marine organisms³¹¹ and in foods³¹² are available.

It is less well-known that certain natural sulfur-rich crude oils as well as soils also contain organic polysulfanes which are not of biological origin but the result of nonenzymatic incorporation of sulfur into functionalized organic compounds.^{313,314} These systems will be discussed in Section VI.C.

B. Organic Polysulfanes of Biotic Origin

1. Chain-Like Polysulfanes

Table 5 summarizes some of the chain-like polysulfanes R-S_n-R which have been identified as components of various organisms, natural products, or materials prepared from them.³¹⁵⁻³²⁵ The sulfur chain length varies between 2 (not shown) and 6, while the organic residues R are saturated or unsaturated alkyl groups, aryl groups, or derivatives thereof.

More than 40 sulfur compounds have been found in a pentane extract of the durian fruit (*Durio zibethinus* Murr.), which is known for its unpleasant smell. In the Far East, its pulp is eaten or used as a flavor for ice-cream and fruit juice. Among the products identified by GC-MS after flash chromatography were the symmetrical and unsymmetrical methyl, ethyl, propyl, and isopropyl trisulfanes.³²⁴

Asafoetida is the oleogum resin exudate obtained from certain *Ferula* species. It has a characteristic strong odor and is used as a flavoring in a variety of foods. The volatile oil obtainable by steam distillation is abundant in sulfur compounds. The flavor of

asafoetida is largely due to 2-butyl-1-propenyldisulfane, 1-methylthiopropyl-1-propenyldisulfane, and 2-butyl-3-methylthioallyldisulfane, but in addition the four tri- and tetrasulfanes mentioned in Table 5 have been identified as minor components by GC-MS analysis.³¹⁷

The edible Shiitake mushroom (*Lentinus edodes*) is another rich source of cyclic and noncyclic sulfur compounds. Blending of the fresh mushrooms with water at pH 7, followed by pentane extraction and GC-MS analysis of the extract, showed Me₂S₃ as one of the major constituents (besides various disulfanes).³¹⁶ When the blending was carried out at pH 9.0, at which enzymes have their maximum activity, additional sulfur compounds such as Me₂S₄ and cyclic species (see below) could be extracted and detected by GC-MS.³¹⁶ This result clearly shows that the workup procedure does influence the kind of products to be detected.

A large number of organic sulfur compounds have been detected in extracts, distillates, or steam distillates prepared from garlic, onions or other Allium species. This chemistry has been expertly reviewed by Block.³¹⁸ Polysulfanes have been detected in many of these preparations, but more recent results show that fresh extracts of garlic, prepared under mild conditions (20 °C), did not show any polysulfanes R-S_n-R, with n > 2, when analyzed by reversed-phase HPLC analysis.³¹⁸ It has in fact been shown that the complex mixture of acyclic and heterocyclic polysulfanes in the essential oil of garlic as reported earlier is a consequence of the action of heat during the steam distillation process on the natural products allicin and diallyldisulfane.³²⁶

However, commercial garlic oil, prepared by steam distillation of garlic homogenizates, does contain diallyltri-, tetra-, penta-, and hexasulfane as well as the corresponding dimethyl and methylallyl derivatives,^{318,327} determined by HPLC and GC-MS analysis (Table 5). The concentrations of these polysulfanes R₂S_n (n > 2) decrease with the number of sulfur atoms in the molecule. Detailed investigations revealed that the diallylpolsulfanes probably originate from the very reactive diallyldisulfane by thermal cleavage of the S-S and C-S bonds and recombination of the RS· and RSS· radicals as well as by interconversion reactions of the type shown in eq 179. The diallylpolsulfanes exhibit antimicrobial activity

which, in the case of *Heliobacter pylori*,³²⁸ *Staphylococcus aureus*, methicillin-resistant *S. aureus*, three *Candida* spp., and three *Aspergillus* spp.,³²⁹ increases with the number of sulfur atoms. *Heliobacter pylori* is the causal agent of chronic gastritis as well as of gastric and duodenal ulcers.



When homogenates of garlic are extracted by methanol, allylmethyltrisulfane can be detected in the extract.³¹⁸ Unsaturated polysulfanes from *Allium* species inhibit the growth of certain tumors.³¹⁸

Tri- and tetrasulfanes with the unusually long, oxidized alkyl chain $C_8H_{17}-CO-C_2H_4-$ (3-oxoundecyl) as substituents have been isolated as colorless needles from methanol/chloroform extracts of a Hawaiian alga (Table 5) by LC on silical gel and gel permeation chromatography, followed by crystallization.³²⁰ These compounds were characterized by ¹H NMR, MS, and UV spectroscopy.

It also should be mentioned that dialanyltrisulfane and, to a smaller degree, the corresponding tetrasulfane have been detected in acidic wool hydrolysates, but it is not clear whether the related amino acid $[HOOC-CH(NH_2)-CH_2]_2S_3$ is part of the wool structure or is formed from cystine during hydrolysis.³¹⁹ [In the biochemical literature, dialanyltrisulfane is often incorrectly termed as "cysteine trisulfide".]

The origin of dimethyltrisulfane discovered in disrupted cabbage tissue has been studied, and it was found that the trisulfane is most probably formed by reaction of hydrogen sulfide with methyl methanethiosulfinate (dimethyldisulfane-1-oxide) and/or methyl methanethiosulfonate (dimethyldisulfane-1,1-dioxide), which both originate from *S*-methyl cysteine sulfoxide by the action of a C-S lyase.³³⁰

A natural peptide containing a trisulfane group instead of a disulfane bridge has been isolated from genetically engineered *Escherichia coli* bacteria.³³¹ It is a derivative of the human growth hormone consisting of 191 amino acids in a single chain with a trisulfane bridge between the cysteine (alanyl) residues no. 182 and 189. This result has been confirmed by mass spectrometry.³³² A trisulfane structure has also been observed in recombinant DNA-derived methionyl human growth hormone in the bridge between cysteine residues nr. 53 and 165 using tandem mass spectrometry and exact mass determination.³³³ The transformation of a peptide containing two cysteine residues in their SH form into cyclic derivatives with di-, tri-, tetra-, and pentasulfane groups by treatment with bis(tetrabutylammonium) hexasulfide has been reported.³³⁴

Calichecin γ_1 ³³⁵ and the esperamicins A₁, A₂, and A_{1b}³³⁶ contain the MeSSS- group attached to a complex structure. These natural products are very potent antitumor antibiotics.

2. Cyclic Polysulfanes

Lenthionine (1,2,3,5,6-pentathiepane) was the first cyclic polysulfane isolated from an organism. However, in the very first report, it was stated that this compound is not present in Shiitake mushrooms but


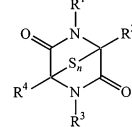

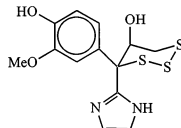


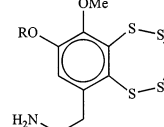


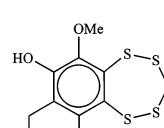
is formed from an unknown precursor by the action of an enzyme when the mushroom was immersed in water overnight.¹²³ From 5 kg of dried mushrooms, 0.44 g crystalline lenthionine (mp 61 °C) was obtained; its structure (see Table 6) was established by mass spectrometry¹²³ and X-ray diffraction on a single crystal.²²³ In addition, hexathiepane (Table 6) and 1,2,4,6-tetrathiepane were also isolated from the aqueous preparations of *Lentinus edodes* mushroom.¹²³ All three cyclic methylene sulfides can easily be synthesized from CH_2Cl_2 and aqueous sodium polysulfide.¹²³ When fresh *Lentinus edodes* was directly extracted by chloroform (which inactivates the enzymes) and the extract fractionated by LC on silica gel and analyzed by GC-MS or MS, the only polysulfanes detected were dimethyltrisulfane, 1,2,3,5-tetrathiane, and lenthionine.³¹⁶ However, when the fresh mushrooms were blended at room temperature with water for 3 min with the pH adjusted to 9.0, chloroform extraction yielded 18 organic sulfur compounds, including the ones mentioned above.³¹⁶ They all are believed to originate from lenticic acid by enzymic activity via CH_2S_2 as a reactive intermediate.^{178,316}

Lenthionine and related cyclic methylenedisulfanes of ring sizes 6–12 have also been obtained from the alga *Chondria californica* and from the seed of the mimosacea *Parkia speciosa*.^{337,338}

Derivatives of 1,2,3-trithiane as well as 1,2-dithiolane are known for their biological activity.^{310,339} Three naturally occurring trithiane derivatives are shown in Table 6. 5-Methylthio-1,2,3-trithiane has been isolated by gas-phase isopentane extraction from the green alga *Chara globulares* and identified by GC-MS, ¹H NMR and UV spectra.³⁴⁰ Its synthesis is straightforward.³⁴⁰ The second natural trithiane derivative has been extracted by methanol/water from the New Zealand ascidian *Aplidium* sp. D and isolated after HPLC as a yellow gum.³⁴¹ This compound, which has also been obtained from the ascidian *Hypsistozoa fasmeriana*,³⁴² shows antimicrobial, antileukemic, and cytotoxic properties in vitro.³⁴¹ Finally, 1,2,3-trithiane-5-carboxylic acid has been isolated from the lower parts of asparagus shoots by extraction with ethanol and ion-exchange chromatography.³⁴³

Two cyclic polysulfanes called lissoclinotoxin A and B have been obtained by methanol extraction of the tunicate *Lissoclinum perforatum*, followed by preparative HPLC on silica gel (Table 6). Lissoclinotoxin A forms a beige powder of mp 245–250 °C.³⁴⁴ Originally, lissoclinotoxin A was thought to be a benzo-1,2,3-trithiane derivative, but later it was shown that it is a pentathiepin; the same holds for lissoclinotoxin B, which forms a yellow powder.³⁴⁵ In vitro, these compounds exhibit potent antimicrobial, antifungal, and modest cytotoxic activities.^{344,345} Varacin, another benzopentathiepin derivative (Table 6), has also been obtained from a tunicate; it exhibits cytotoxic and antifungal, but no antimicrobial activity. These compounds bear obvious structural and biosynthetic relationships to dopamine.³⁴⁶ The synthesis of varacin and its derivatives from vanillin³⁴⁷ and from 3,4-dimethoxyphenethylamine³⁴⁸ has been reported. Struc-

Table 6. Naturally Occurring Cyclic Bis-organyl Polysulfanes

Compound	Source	Ref.	Compound	Source	Ref.
 5-Methylthio-1,2,3-trithiane	<i>Chara globularia</i> (green alga)	340			
 5-Carboxyl-1,2,3-trithiane	<i>Asparagus officinalis</i>	343	3,6-Epipolythiopiperazine-2,5-dione n = 3; R ¹ = R ³ = Me; R ² = CH ₂ OH; R ⁴ = CH ₂ Ph	Fungus <i>Pithomyces chartarum</i>	183, 191, 350
	<i>Aplidium</i> sp. D. (ascidian)	341	Sporidesmine E n = 4; R ¹ = R ³ = Me; R ² = CH ₂ OH; R ⁴ = CH ₂ Ph	<i>Hyalodendron</i> sp. (fungus); <i>Penicillium turbatum</i>	351
 Lenthionine	<i>Chondria californica</i> (red alga) <i>Parkia speciosa</i> (mimosaceae species) <i>Lentinus edodes</i> (Shiitake mushroom)	311, 337 338 123, 223, 316	Sporidesmine G	<i>Pithomyces chartarum</i>	183, 191
 Hexathiepane	<i>Lentinus edodes</i> (Shiitake mushroom)	123, 316			
 Hexathionane			R = H: Lissoclinotoxin A	<i>Lissoclinum perforatum</i> (ascidian)	344
 1,2,3,5-Tetrathiane			R = Me: Varacin	<i>Lissoclinum vareau</i> (ascidian)	346
					
			Lissoclinotoxin B	<i>Lissoclinum perforatum</i>	345

turally related benzopentathiepins have also been isolated from *Lissoclinum* species.³⁴⁹

Sporidesmin is a naturally occurring polycyclic disulfane which contains the piperazinedione ring shown in Table 6. The corresponding trisulfane has been termed sporidesmin E. It was obtained by extraction of *Pithomyces chartarum*, followed by LC on silica gel.¹⁹¹ From the same organism, sporidesmin G, the corresponding tetrasulfane, was obtained.¹⁸³ These compounds are also biologically active but obviously less well studied in this respect.

The piperazinedione framework is also present in hyalodendrin, which is a cyclic disulfane with the substituents given in Table 6. The corresponding trisulfane has been isolated from cultures of an unidentified fungus,³⁵⁰ while the tetrasulfane was obtained from chloroform extracts of fermentations of *Hyalodendron* sp.;³⁵¹ it is also produced by *Penicillium turbatum*.³⁵¹ In all cases, however, it is unknown whether these polysulfanes are present in the organisms or result from the workup procedure by decomposition of the corresponding disulfane. Such conversion reactions have in fact been observed.³⁵¹

C. Organic Polysulfanes of Abiotic Origin

All fossil fuels contain sulfur but the concentrations vary from traces to more than 10 wt %; this sulfur is bound in diverse molecular structures. In general, the quantity and molecular composition of sulfur compounds in crude oils reflect the corresponding properties of the source rock from which they were gener-

ated. The sulfur content of the source rock *kerogen* may reach or even slightly exceed 14% (kerogen is the macromolecular component of consolidated sedimentary organic matter that is insoluble in common organic solvents).³⁵² Some of this sulfur is assumed to be present as polysulfane cross-links throughout the molecular network. Polysulfane linkages in kerogen may influence the rate of petroleum generation from source rocks since S-S bonds are more easily cleaved than carbon-associated bonds. The sulfur content in crude oils varies from 0.05% to more than 14%, but few commercial crude oils exceed 4%. Oils with less than 1% sulfur are classified as low-sulfur, and those above 1% as high-sulfur. For obvious reasons the industry prefers to refine low-sulfur crudes. The world's potential reserves of high-sulfur oils, however, greatly exceed the known reserves of the presently produced low-to-moderate-sulfur crudes. Use of these sulfur-rich resources will be required more and more to meet future energy demands.³⁵³

It is unlikely that organic sulfur of biosynthetic origin can account for all the organically bound sulfur present in sedimentary and fossil organic matter since the concentration of sulfur in biomass is usually below 2 wt %.³⁵⁴ Furthermore, the ³⁴S/³²S ratio of sulfur in fossil and sedimentary organic matter is enriched with the lighter isotope by >10% relative to that in the biomass.³⁵⁵ Thus, it is generally accepted that the major fraction of the organically bound sulfur in fossil organic matter is formed through geochemical pathways. Unfortunately, due to the polymeric nature of the material discussed, it

is by no means straightforward to elucidate the exact structural units in sulfur-rich fossil matter. For this reason, the geochemical pathways for incorporating sulfur into sedimentary organic matter are also not completely understood. However, it is becoming increasingly clear that reactions between functionalized organic compounds and reactive inorganic species such as H₂S and polysulfide ions are mainly involved. This view is supported by the results of model reactions between saturated or unsaturated aldehydes and ketones as well as unsaturated hydrocarbons with hydrogen sulfide or polysulfide anions.^{356–358} For example, 2-nonanone, nonanal, cholestan-3-on, and phytalen on reaction with an aqueous NaHS/S₈ mixture (20:1) at 50 °C using a phase-transfer catalyst formed significant amounts of compounds in which the oxo group was replaced by a polysulfane moiety with up to three sulfur atoms in the chain or ring formed (>C=O → >CH–S–S–...),³⁵⁹ In a similar fashion, isoprenoid polysulfanes are formed by low-temperature reactions of the CC double bonds of phytol and phytadienes with inorganic polysulfides.³⁶⁰

Spectroscopic and other studies of the sediments in the Bay of Conception off the coast of Chile showed organic polysulfanes to constitute the major fraction of the organic sulfur present. In these habitats (1–3 cm below the surface of the sediments) H₂S is formed by bacterial sulfate reduction, and its partial oxidation produces inorganic polysulfides which are strong nucleophiles able to attack many organic compounds.³⁶¹ For a review on organically bound sulfur in the geosphere, see ref 362.

Dimethyldi-, tri-, and tetrasulfane have also been detected in the gas phase of the Hamburg sewage pipe system by GC-MS analysis but their origin is unclear.³⁶³ Such compounds will indirectly contribute to the severe corrosion of the concrete pipes of this underground system since sulfur bacteria like *Thiobacilli* oxidize polysulfanes equally well to sulfuric acid, as in the case of hydrogen sulfide.

VII. Applications of Organic Polysulfanes

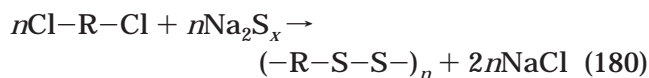
For many years organic polysulfanes have been used as additives to high-pressure lubricants to prevent metals from welding together under extreme pressure (EP).³⁶⁴ At temperatures above 200 °C, the metals react with the EP additive to form metal sulfides which have a lower friction coefficient as well as a lower melting point than the metals themselves that prevents the cold welding under EP conditions. In addition, the additives owing to their polar nature show a higher adsorption strength on the metal surface compared to that of mineral oils. Such EP additives are produced by sulfurization of hydrocarbons or of natural oils (e.g., rape seed oil) or fatty esters including triglycerides with elemental sulfur. They are sometimes marketed under the name "sulfur carrier".³⁶⁵

Organic polysulfanes are important constituents of polysulfide polymers of the Thiokol type, of vulcanized rubber, and of sulfur cement. In addition, there are a few special applications in the oil producing industry and in medicine. Sulfur containing polymers

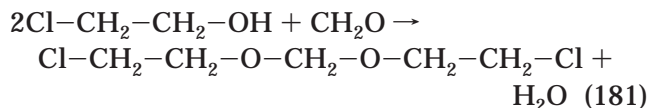
have been extensively reviewed by Tobolsky and MacKnight in 1965³⁶⁶ and by Duda and Penczek in 1987.³⁶⁷

A. Polysulfide Polymers

The preparation, properties, and uses of industrially produced polysulfide polymers have been reviewed in detail by Ellerstein and Bertozzi in 1982 and by Lucke in 1992.³⁶⁸ The synthesis is based on the reaction of aliphatic dichloro compounds with aqueous sodium polysulfide according to eq 180:

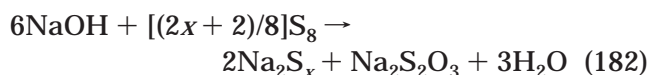


Most of the polysulfide polymers are made from bis-(2-chloroethyl)formal [bis(2-chloroethoxy)methane], which is synthesized from ethylene chlorohydrin [1-chloroethane-2-ol] and formaldehyde under acid catalysis according to eq 181:

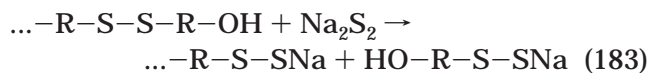


Ethylene chlorohydrin is made from HCl and ethylene epoxide C₂H₄O (oxirane). When small amounts of 1,2,3-trichloropropane are added to the bis(2-chloroethyl)formal obtained by reaction 181, some branching of the otherwise linear polymer structure is achieved.

The sodium polysulfide solution is customary made by heating concentrated aqueous sodium hydroxide with elemental sulfur to 100–150 °C according to eq 182:



The thiosulfate byproduct does not take part in the subsequent reactions with the organic chlorides. The *x* value in eq 182 is referred to as the rank of the sodium polysulfide; a typical value for *x* is 2.25. However, since aqueous sodium polysulfide is a complex mixture containing various polysulfide anions in equilibrium, the final polymer obtained in reaction 180 may contain various structural units S_{*n*} (*n* = 1–4). In addition, the aqueous phase contains OH[–], resulting in some terminal OH groups in the polymer. By applying an excess of sodium polysulfide (1.3 mol per mol Cl–R–Cl), the number of chain-terminating OH groups is reduced:



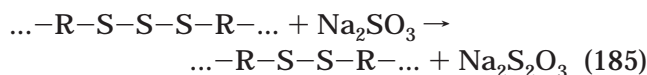
At the end of the polymerization process, the polymers are washed free of sodium chloride, of excess sodium polysulfide, and of solubilized hydroxyl-containing terminals. The molecular mass of the resulting polymer is thought to be at least 5 × 10⁵–10⁶; the yield is 80%. The polymer forms as small dispersed spheres approximately 5–15 μm in diameter, which have a higher density than the aqueous

phase in which they are produced and therefore settle to the bottom of the reactor. The polymer is washed with hot water, followed by decantation, coagulation by acidification, and drying by heat, resulting in a solid, rubbery mass.

If a liquid polysulfide polymer (LP) is wanted, a chemical reduction of some of the polysulfide groups to thiol terminals is carried out, after which the polymer is cleaned, coagulated, and dried to its final liquid form. The thiol-terminated version is by far the most common form of polysulfide polymers (molecular mass 700–8000; trade name LP Thiokol). A mixture of NaSH and Na₂SO₃ is used to generate terminal SH groups from disulfane structural units:



The sulfite not only helps in the reduction of the disulfane unit to two thiol groups, but it also removes the polysulfanes of rank greater than 2:



The polymer is then in a stripped state in which no polysulfane group exceeds the disulfane stage. Thiokol FA is a copolymer of dichloroethane and of the bis-(2-chloroethyl)formal-sodium polysulfide reaction product.

The polysulfide polymers derive their utility from their unusually good resistance to solvents and to the environment and their good low-temperature properties. The solid elastomers in the vulcanized cure state are used in printing rolls, paint-spray hose, solvent hose, gaskets, and gas-meter diaphragms. The liquid polysulfide polymers are used mainly in sealants. The largest application is sealants for double-pane insulating glass windows. Other applications are general sealants and high-quality sealants for building construction, boat hulls and decks, printing rolls, aircraft integrated fuel tanks, and aircraft bodies. The common way to convert the liquid polysulfide polymers to solid elastomers is to oxidize the terminal thiol groups to disulfanes. This is usually carried out in a formulation with fillers, plasticizers, and curing-rate modifiers (e.g., stearic acid). Both organic oxidizing agents, e.g., *tert*-butylhydroperoxide, and inorganic oxidizing agents have been used, with most cures occurring at ambient temperature in a few hours.

The reactions of di-, tri- and tetrabromooctane with ammonium polysulfide yields polysulfane polymers which have been studied as model compounds for the polysulfanes suspected in sulfur-rich fossil fuel.³⁶⁹

B. Vulcanization of Rubber by Sulfur

By far the most important industrial application for organic polysulfanes is the vulcanization of natural and synthetic rubber by elemental sulfur. More than 10⁵ tons of sulfur are used for this process annually. A typical vulcanization mixture (called "compound") consists of rubber (100 parts), carbon black (50 parts), zinc oxide (2–10 parts), stearic acid (1–4 parts), sulfur (0.5–4 parts), an organic ac-

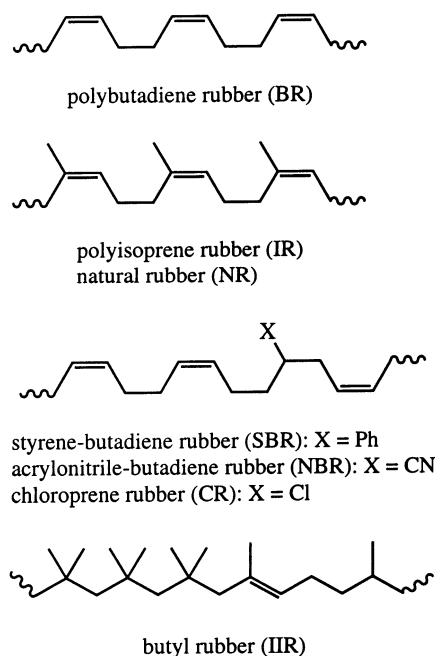


Figure 6. Polymeric alkenes which are vulcanized by elemental sulfur or sulfur donors.

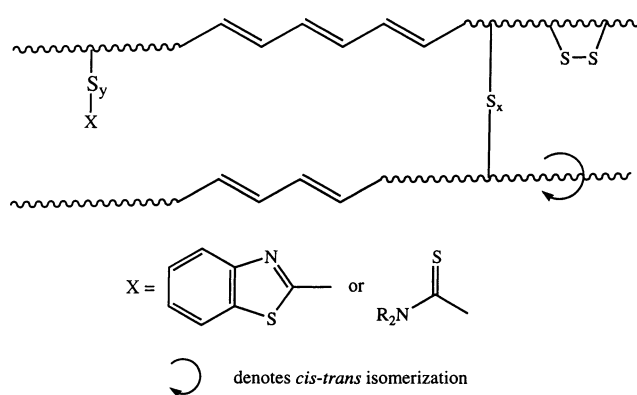
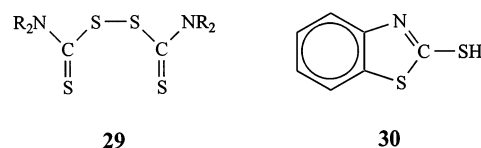


Figure 7. Schematic representations of rubber after vulcanization by sulfur, resulting in pendant groups ($-S_y-X$) as well as in mono-, di-, and polysulfane bridges.

celerator like tetramethylthiuramdisulfane (TMTD) **29** or 2-mercaptobenzothiazole (MBT) **30** (0.5–2 parts), and antioxidants as well as retarders (1–2 parts) to control the reaction and to improve the performance of the product during service.³⁷⁰ The organic polymers to be vulcanized contain alkenic double bonds in varying environments; see Figure 6.



The vulcanization process ("curing" by heating to 140–150 °C) results in organic mono-, di-, and polysulfanes, some of which act as cross-links between the polymer chains and thus generate the high-elastic properties of vulcanized rubbers (see Figure 7). The rather complex chemistry of vulcanization and the importance of polysulfane cross-links have been reviewed several times.^{371–375} However,

it should be recognized that rubber mixtures are difficult to analyze chemically because of their polymeric nature. Therefore, the chemistry of vulcanization has been worked out largely by using low-molecular mass analogues of the rubber structure (model alkenes) and extrapolating the results to the polymeric system. These studies have considerably increased the general knowledge about organic polysulfanes^{133,367,376–378} but the exact mechanism of the rubber vulcanization by sulfur or sulfur-donors is still far from being completely understood. For an excellent review on the model-compound vulcanization studies, see Nieuwenhuizen et al.³⁷⁹

The quantitative determination of mono-, di-, and polysulfanes during the curing process has first been attempted by the application of a variety of chemical probes such as triphenylphosphane for cross-link shortening, di-*n*-butyl phosphite for cleaving di- and polysulfane cross-links, and a thiol-amine reagent which cleaves only polysulfanes.³⁸⁰ From these studies it is known that polysulfanes form first during curing and are then degraded to di- and monosulfanes.³⁸¹ TMTD is known to react with elemental sulfur on heating to a mixture of the corresponding polysulfanes (TMTP).⁷³

More recently, however, it has been possible to observe the vulcanization process as well as the thermal and oxidative aging of the vulcanized rubber more directly by X-ray near edge absorption structure (XANES) spectroscopy (see Section IV.E).²⁷¹ This method allows the identification and to a certain degree the determination of S–S bonds in disulfane units compared to polysulfane units as well as of C–S bonds linked to either the rubber polymeric chain or to a pendant group resulting from the reaction of the sulfur with a molecule of an accelerator (X in Figure 7). Slightly different excitation energies for the promotion of a sulfur 1s electron to one of the antibonding orbitals of the mentioned bonds are observed for these cases which under high-resolution conditions can be resolved. Larger differences in the energies are observed if the sulfur atom is at a different oxidation state as in sulfoxides or sulfates. In this way the oxidative aging of vulcanized rubber can be followed.³⁸² Time-resolved XANES measurements revealed that the polymerization process starts with the formation of polysulfane units, which later are degraded with formation of disulfane and monosulfane units. Even overvulcanization and reversion processes can be observed (cross-link shortening, formation of zinc sulfide, changes in the coordination sphere of the C–S bonds). Polysulfanes are formed in rubber–sulfur mixtures even before external heating as a result of the mixing (“compounding”) procedure.³⁸³ However, since specific polysulfanes have never been identified as components of the real rubber mixture during curing, the reader is referred to the cited literature for more details on the chemistry of these systems.

C. Sulfur Cement and Sulfur Concrete

Elemental sulfur is an inexpensive material available in high purity and large quantities. It has repeatedly been suggested that “new uses” of sulfur

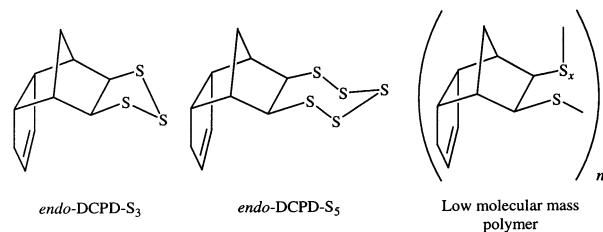


Figure 8. Polysulfanes formed in the reaction of dicyclopentadiene with elemental sulfur at elevated temperatures.

in the civil engineering field may be found. For example, sulfur is used as an extension to asphalt in road pavements and as an insulating material.³⁸⁴ Application as a cheap construction material requires “modification” by additives designed to stop the embrittlement which occurs with pure elemental sulfur. If pure liquid sulfur is cooled to ambient temperature, monoclinic octasulfur (β -S₈) is instantaneously formed which then slowly converts to orthorhombic α -S₈. Because of the difference in densities between α - and β -S₈, a brittle material results. Many additions have been proposed to modify elemental sulfur, nearly all of them are either organic polysulfanes or substances which will react with liquid sulfur to give in situ formation of polymeric polysulfanes, e.g., alkenes and certain Thiokols.³⁸⁵

The most important alkene in this context is dicyclopentadiene (DCPD) or a mixture of di- and tricyclopentadienes. These are inexpensive refinery products. The addition of 5–10% DCPD by mass to elemental sulfur, followed by carefully controlled heating to 140 °C, results in a complex mixture of polysulfanes and sulfur which after cooling to 20 °C is no longer brittle but of extremely high mechanical strength. This material is known as sulfur cement. When the liquid sulfur cement is mixed with suitable preheated mineral fillers, a very useful construction material is obtained on cooling to ambient temperature; this material is called sulfur concrete.³⁸⁵ In contrast to Portland cement and conventional concrete, sulfur cement and sulfur concrete are resistant to aqueous acids and concentrated salt solutions.

The polysulfanes formed on reaction of DCPD with liquid sulfur have been studied by extraction of sulfur cement and analysis by LC, ¹H NMR, MS, and other techniques.^{367,385–387} The initial products are the trisulfane and the pentasulfane derived from DCPD by addition of S₃ or S₅ units to the norbornenyl double bond. These “monomers” are believed to further react with elemental sulfur to form low-molecular mass polymers (CS₂ soluble) and on further heating form insoluble material. The cyclopentenyl unsaturation of DCPD is much less reactive and is still present in the CS₂ soluble products. *endo*-DCPD reacts more slowly with liquid sulfur at 140 °C than *exo*-DCPD, while the cyclic trisulfanes of *endo*- and *exo*-DCPD react at almost the same rate with liquid sulfur at 140 °C.^{386,387} The structures of DCPD-S₃, DCPD-S₅, and the likely structure of the low-molecular mass polymer are shown in Figure 8. Polysulfanes prepared from DCPD have also been used as sulfur donors in the sulfur-vulcanization of rubber;³⁸⁸ see Section VII.B.

The reaction of styrene with liquid sulfur also results in the formation of polymeric polysulfanes.^{367,386} Recently, sulfur cement has been used to seal mercury containing waste from gold mining processes by mixing the liquid mercury with the cement and melting the mixture in a heated vessel. This treatment turns the mercury metal into insoluble mercury sulfide. After solidification of the mixture in a mold, the mercury is immobilized.

D. Organic Polysulfanes as Antiradiation Drugs

Field et al.³⁸⁹ discovered that certain organic di- and trisulfanes R-S_n-R' terminated by sulfinate functions -SO₂⁻ protect mice against otherwise lethal effects of ionizing radiation. The preparation of these compounds has been described in Section II.A.13. The ionic sulfinate group makes these compounds partly hydrophilic and water soluble. Neither a trisulfane nor a sulfinate by itself is significantly radioprotective, but the presence of a sulfur-sulfur bond is considered a key requirement since a thiol can be engendered by a neighboring group effect of an electron-donating group. A hypothesis says that this "protective thiol" undergoes formation of mixed disulfanes with proteins in the cells leading to a series of disturbances including decreased oxygen consumption, decreased carbohydrate utilization, and mitotic delay by temporary inhibition of DNA and RNA synthesis, along with cardiovascular, endocrine, and permeability changes. The mitotic delay allows time for repair processes to restore normal nucleic acid synthesis.³⁹⁰

Acknowledgments. I am grateful to my wife Dr. Yana Steudel for taking care of the graphical part of this review and to my co-workers whose names appear in the references for their contributions. I also acknowledge the valuable recommendations by three anonymous reviewers. Our research on organic polysulfanes and other sulfur-rich compounds has been supported for many years by the Deutsche Forschungsgemeinschaft and the Verband der Chemischen Industrie.

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