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The chemistry of disulfides

I V Koval'

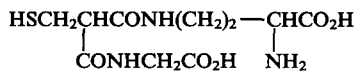
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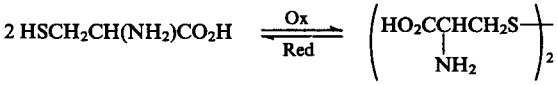
Abstract. The results of studies in the chemistry of disulfides during recent years are surveyed and treated systematically. The structures, methods of synthesis, and the physicochemical and chemical properties of disulfides are examined. The bibliography includes 151 references.

I. Introduction

Disulfides play an important role in living organisms. In the formation of the tertiary structure of proteins, covalent disulfide bonds are known [1] to ensure the formation of cross-links, which are much stronger than hydrophobic interactions and hydrogen bonds. The disulfide cross-link renders relatively permanent the disposition of the peptide chains established initially as a result of weaker bonding forces. The biochemical importance of the disulfide bond is also determined by the uniqueness of the nature of the thiol–disulfide system, in which the S–S bond can be formed under conditions appropriate for biological processes — via disulfide exchange with participation of glutathione. [2]

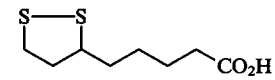


Cystine, which contains a disulfide bond, is a component of aerobic systems. [1] It is formed as a result of the ready oxidation of cysteine.



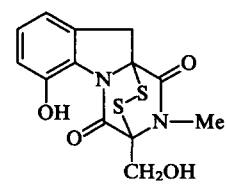
In the hormone insulin, the disulfide bonds of cystine join two different peptide chains, one of which contains 21 and the other 30 aminoacid residues. [1] The composition and form of the protein of hair are to a large extent determined by the cystine S–S bonds and the chemical permanent wave in hair is based on this fact. [1] Hair is initially treated with a reductant in order to cleave the S–S bonds and convert them into sulfhydryl groups. Hair, the proteins of which no longer have cross-links, readily assumes the required form by virtue of the regeneration of the protein S–S cross-links as a result of oxidation by air or a chemical oxidant, and retains it for a long time.

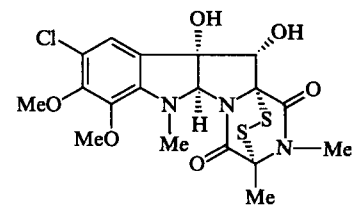
Lipoic acid



participates in the oxidative decarboxylation of α-oxoacids and is a common unit in two fundamental biochemical processes in which the thiol–disulfide system participates: electron transfer and generation of thioester linkages. [2,3]

Disulfides such as glyotoxin and sporidesmin





are the main representatives of the group of metabolites of fungi. [1] Many disulfides enter into the composition of various natural products. For example, (−)-bis(3-acetoxyundec-5-enyl) disulfide has been isolated from Hawaiian seaweed of the genus *Dictyopteris*. [4] Di-n-propyl disulfide is a component of the mixture of substances responsible for the specific smell of the onion. [2]

Certain disulfides can be used as accelerators of the vulcanisation of rubber, [5] as chain transfer agents in radical polymerisation processes, [6] as biologically active substances, [7] and as complex-forming agents. [8] A very important application of disulfides is in fine organic synthesis. The lability of the S–S bond in disulfides and its ability to be cleaved by both nucleophiles and electrophiles as well as the active reaction centre with a variable valence (sulfur) impart to disulfides the properties of extremely valuable synthons, which are widely used in multistage organic syntheses and in particular for the introduction of the sulfide functional group.

The interest shown by many investigators gave rise at one point to the appearance of a series of reviews [2,3,9–15] reflecting to some extent the state of the chemistry of disulfides during that period. Unfortunately, the reactions occurring with an increase in the valence of sulfur and in particular the oxidative imination reactions and the formation of sulfonium complexes were hardly considered in these communications. On the other hand, since the publication of these reviews many new experimental data on

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the chemistry of disulfides have accumulated and these are surveyed in the present review. The literature is covered up to 1992 inclusive.

II. The structure and physicochemical properties of disulfides

Virtually all the possible physicochemical research methods have been used in the study of the structure of disulfides and also of the main characteristics of the S–S bond in disulfides.[2,3,15–17] In particular, it has been established[2,15,16] that the molecules of disulfides have a zig-zag shape with a X–S–S–X dihedral angle of ~90°.

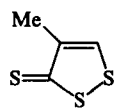
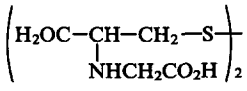
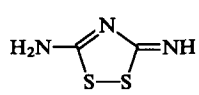
The strongest bonds between two identical atoms are formed by Group V–VII elements of the Third Period, which has been explained[17] by the contribution of the $p-\pi$ and $d-\pi$ interactions. By virtue of these interactions, the S–S bond in disulfides is much stronger than the O–O, Se–Se, and Te–Te bonds in the isostructural peroxides, diselenides, and ditellurides. The S–S bond dissociation energies for certain disulfides are listed in Table 1.

Table 1. The S–S bond dissociation energies.[3,17]

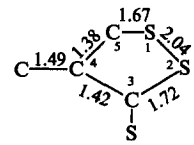
Disulfide	E_{dis}/kcal mol^{-1}
PhS–SPh	55.0 ± 1.5
FS–SF	60.0 ± 4.0
PhS–SMe	65.0 ± 1.5
HS–SH	66.0 ± 2.0
EtS–SEt	70.0 ± 2.0
EtS–SMe	72.0 ± 2.0
MeS–SMe	74.0 ± 2.0

As can be seen from the data in Table 1, the structures of the alkyl groups linked directly to sulfur in disulfides have little influence on the strength of the S–S bond. Aryl groups exert a greater influence on the strength of the bond, which has been explained by the involvement of the sulfur p electrons in conjugation with the π electrons of the benzene ring (p,π conjugation). The enthalpy of the S–S bond is 63 kcal mol^{-1}. The S–S bond lengths in certain disulfides are listed in Table 2.

Table 2. The S–S bond lengths.[3]

Compound	S–S bond length/Å
	2.03
MeS–SMe	2.04
	2.04
HS–SH	2.04
ClS–SCl	2.05
CF_3S-SCF_3	2.05
	2.09

By comparing the S–S bond lengths in Table 2 with the values calculated by Pauling's equation,[3] it is possible to estimate the amount of double-bond character in the S–S bond. In 4-methyl-1,2-dithiacyclopent-4-ene-3-thione, it amounts to 20%, which indicates the aromatic nature of such trithione compounds and hence their high stability, which is also indicated by the results of the structural analysis of 1,2-dithiolane-3-thione.



The C(5)–S(1) bond (1.67 Å) in 4-methyl-1,2-dithiacyclopent-4-ene-3-thione is much shorter than the usual C–S bond (1.83 Å), while the C(4)–C(5) bond (1.38 Å) has virtually the same length as the C–C bond in aromatic hydrocarbons.

The structure of the terminal alkyl groups in disulfides hardly affects their dipole moments, which is apparently associated with the retention of the configuration of the C–S–S–C group.[3] The experimental molecular refractions of certain disulfides are numerically greater than the values calculated from atomic refractions.[3]

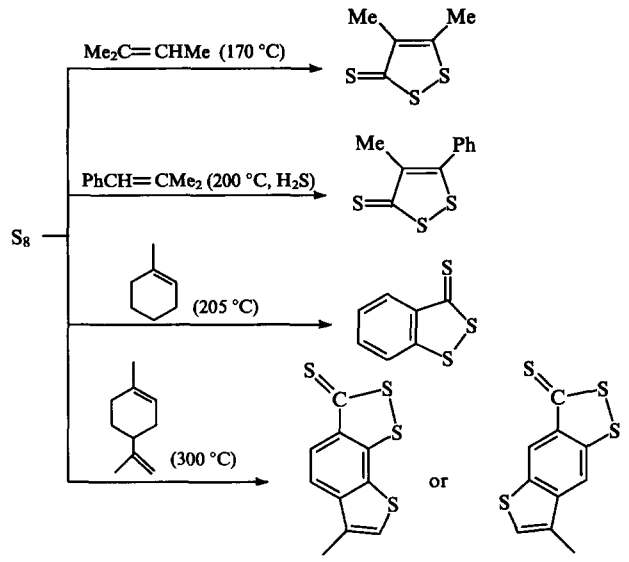
The absorption maximum in the UV spectra of dialkyl disulfides is in the range 240–280 nm. It undergoes a hypsochromic shift on passing from Me to Et, to Pr^i, and then to Bu^t, which is believed[3] to be associated with hyperconjugation. The absorption maximum in the UV spectra of *para*-substituted diphenyl disulfides p-$XC_6H_4SSC_6H_4Y$-p (X = H, Cl, NO_2, MeO; Y = NO_2, MeO) is in the range 240–324 nm (ε = 4.07–4.34). As the electron-accepting properties of the substituents in the benzene ring become more pronounced, a bathochromic shift of the absorption maximum is observed. The S–S bond stretching vibrations in disulfides are manifested in the range 470–503 cm^{-1}.[3] The chemical shift δ of the protons in the H_3C-S group is in the region of 2 ppm and that of the protons in the >CH–S group is in the region of 3.2 ppm.[18] UV irradiation of diphenyl disulfide at −200 °C leads to the formation of a radical product, the EPR spectrum of which is characterised by an axially anisotropic g-factor. This is apparently due to the localisation of the unpaired electron on the sulfur atom in the PhS$^\cdot$ radical. The absorption spectrum of this radical contains bands at 355 and 380 nm and its luminescence spectrum has bands at 374 and 240 nm.[17]

When diaryl disulfides react with strong electron acceptors (aluminium and gallium halides), the S–S bonds undergo homolytic cleavage with formation of the stable radical-complexes $ArS^\cdot \cdot MCl_3$ (Ar = Ph, p-MeC_6H_4, o-$NO_2C_6H_4$, α-$C_{10}H_7$; M = Al, Ga), which are solid deeply coloured substances capable of being stored under a nitrogen atmosphere for a long time.[19] It has been suggested that the donor–acceptor bond in the radical-complex is formed with participation of the lone pair of the sulfur atoms. In contrast to diaryl disulfides, dialkyl disulfides form under similar conditions 1:1 complexes with the above electron acceptors without the homolytic cleavage of the S–S bond. When the radical-complexes react with stronger electron donors, for example with pyridine, the thiyl radical is displaced and forms a disulfide as a result of recombination.

III. Methods of synthesis of disulfides

1. Syntheses based on sulfur and its inorganic derivatives

The use of sulfur in the synthesis of disulfides has been known for a relatively long time.[3] For example, a preparative method of synthesis of bis(p-aminophenyl) disulfide involves the heating of sulfur with aniline. A series of cyclic disulfides have been obtained by heating sulfur with unsaturated hydrocarbons.[3]



One of the preparative methods of synthesis of dialkyl disulfides involves the interaction of sulfur with alkyl iodides and sodium in liquid ammonia.[2]

$$RI + S_8 + 2\,Na \xrightarrow[NaI]{NH_3} RSSR$$

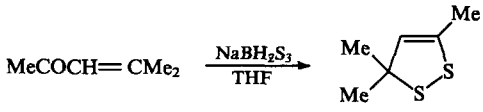
The interaction of elemental sulfur with trialkylboranes and subsequent alkaline hydrolysis of the products also lead to the formation of dialkyl disulfides.[2]

$$R_3B \xrightarrow{S_8\,(\Delta)} RSBR_2 \xrightarrow{OH^-} RSSR$$

On treatment with sulfur-containing sodium tetrahydroborate, aldehydes and ketones are converted into disulfides, while 1,2-epoxides and α,β-unsaturated ketones are converted into bis(1,2-hydroxyethyl) disulfides and cyclic disulfides respectively.[2,20]

$$PhCHO \xrightarrow{NaBH_2S_3} PhCH_2S-SCH_2Ph$$





The interaction of alkyl halides with sulfur in the presence of alkoxides leads to the formation of the corresponding dialkyl disulfides and dialkyl trisulfides.[21]

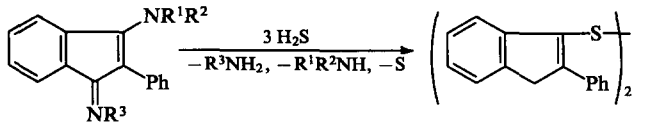
$$RCH_2Hal + S_8 + RO^- \longrightarrow (RCH_2)_2S_n$$

$n = 2, 3.$

The synthesis of alkynyl disulfides based on the reaction of elemental sulfur with lithium acetylides and subsequent sulfenylation of lithium thiolates by sulfenyl chlorides has been described.[22]

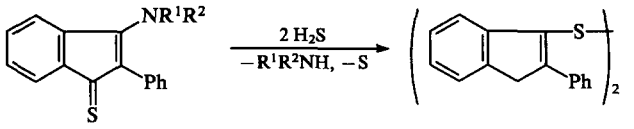
$$RC{\equiv}CLi + S_8 \longrightarrow RC{\equiv}CSLi \xrightarrow[-LiCl]{R^1SCl} RC{\equiv}CSSR^1$$

Among the inorganic derivatives of sulfur, sodium disulfide has found the most extensive application in the synthesis of disulfides. A whole series of preparatively very easy methods of synthesis of dialkyl and diallyl disulfides, described in handbooks and in the scientific literature, have been developed on the basis of the reactions involving the alkylation and arylation of sodium disulfide by alkyl halides and activated aryl halides as well as arenediazonium salts. Dialkenyl disulfides are obtained similarly from sodium disulfide.[23] Among other inorganic derivatives of sulfur, hydrogen sulfide and sulfur monochloride are also used in the synthesis of disulfides. For example, it has been noted[24,25] that bis(indenyl) disulfide is formed in the reaction of hydrogen sulfide with 3-amino-1-imino-2-phenylindenes in an alcoholic medium in the presence of piperidine.

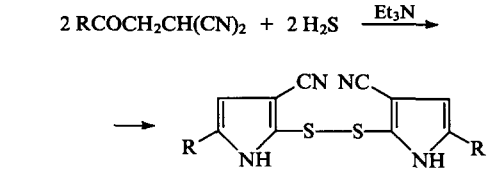


$R^1 = R^2 = H$; R^3 = Alk.

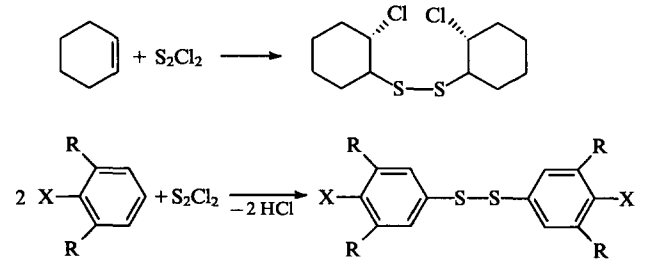
The same disulfide is obtained in the reaction of hydrogen sulfide with 3-amino-2-phenylindene-1-thiones.[25]



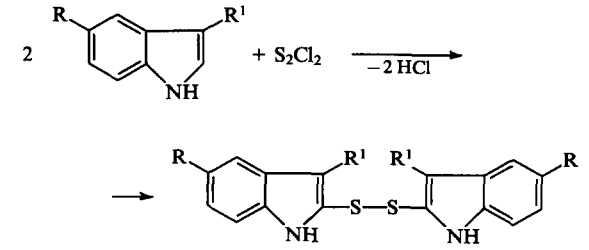
The reaction of hydrogen sulfide with alkyl(aryl) β,β-dicyanoethyl ketones in an organic solvent in the presence of triethylamine affords bis(5-R-3-cyanopyrrol-2-yl) disulfides.[26]



The use of sulfur monochloride in the synthesis of disulfides is based on the reactions involving its addition to unsaturated bonds[27] and also on substitution reactions involving aromatic and heterocyclic compounds.[2,3]



R = H, Bu^t; X = OH, NMe_2.



R, R^1 = Alk.

It has been noted[28] that the interaction of malonic ester with the $SF_4-HF-S_2Cl_2$ system leads to the formation of bis-[di(ethoxycarbonyl)fluoromethyl] disulfide.

2. Synthesis of disulfides from thiols

a. Oxidation of thiols

Thiols are relatively readily oxidised by various oxidants to disulfides. A whole series of preparatively extremely convenient methods of synthesis of disulfides have been developed on the basis of this reaction. The oxidation of thiols by oxygen catalysed by metal ions (Fe^{3+}, Cu^{2+}), UV irradiation, and other initiators of radical processes, is used very often in the synthesis of disulfides. Despite the great importance of this reaction in biological processes and its importance for the removal of sulfur from petroleum products, its mechanism has not been ultimately elucidated.[2] The stoichiometric equation of this reaction in a basic medium is as follows:

$$4RSH + O_2 = 2RSSR + 2H_2O.$$

Flavins oxidise anaerobically the excess thiol to the disulfide in a high yield and are simultaneously reduced to dihydroflavins.[2]

Hydrogen peroxide,[3] iron trichloride,[3] potassium hexacyanoferrate(III),[29] hypohalites,[29] cobalt-disulfophthalocyanine,[29] manganese tris(acetylacetonate),[29] iodine,[30] carbon tetrachloride,[31] *N*-chloro-compounds,[32-34] yeast,[35] and other compounds are also used as oxidants.

b. Photolysis of thiols

In the synthesis of asymmetric disulfides, both individual thiols and their mixtures with disulfides are photolysed. For example, the photolysis of a mixture of ethanethiol and dimethyl disulfide leads to the formation of ethyl methyl disulfide.[36]

$$EtSH \xrightarrow{h\nu} EtS^{\cdot} + H^{\cdot},$$

$$EtS^{\cdot} + Me_2S_2 \xrightarrow{h\nu} EtSSMe + MeS^{\cdot},$$

$$EtS^{\cdot} + MeS^{\cdot} \longrightarrow EtSSMe.$$

c. Sulfenylation of thiols

The sulfenylation of thiols by sulfenyl halides is a preparative method of synthesis of asymmetric disulfides.[29,37-39]

Alkali metal[29] and silver[40] thiolates as well as alkyl(aryl)-thiotrimethylsilanes[41] are sometimes used instead of thiols.

$$RSSiMe_3 + R^1SCl \xrightarrow[-Me_3SiCl]{} RSSR^1$$

R = Ph, $PhCH_2$; R^1 = Et, Ph, 4-MeC_6H_4.

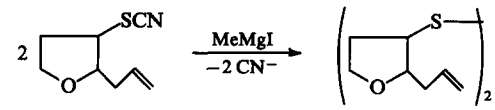
Thiols may be sulfenylated also by sulfenamides,[42-44] carboxylic acid thioloesters,[2] phosphonyl dithioformates,[45] phosphine sulfides,[46] alkyl(aryl)dithiopyridine *N*-oxides,[47] and other divalent sulfur compounds.[48,49] However, these methods have not found extensive application owing to the formation of side products which hinder the isolation of the disulfides.

3. Synthesis of disulfides from thiocyanates

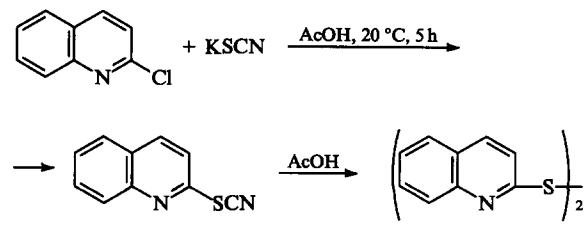
Symmetrical disulfides can be obtained relatively easily by cleaving thiocyanates with alkali.[3]

$$RSCN \xrightarrow{OH^-} RSSR + NH_3 + CO$$

The similar cleavage of 2-allyl-3-tetrahydrofuryl thiocyanate in the presence of methylmagnesium iodide affords bis(2-allyl-3-tetrahydrofuryl) disulfide.[50]



The synthesis of bis(quinolin-2-yl) disulfide by the reaction of 2-chloroquinoline with potassium thiocyanate in acetic acid has been described.[51]



The reaction of thiols with dithiocyanogen affords sulfenyl thiocyanates, the interaction of which with thiols leads to disulfides. This sequence of reactions has been used in the synthesis of cystine derivatives.[29]

$$RSH \xrightarrow[-HSCN]{(SCN)_2} RSSCN \xrightarrow[-HSCN]{R^1SH} RSSR^1$$

$$R = HO_2CCHCH_2;\ NH_2 \qquad R^1 = HO_2CCHCH_2.\ NH_2 \cdot HCl$$

4. Syntheses of disulfides based on tetravalent and hexavalent sulfur compounds

The reduction of sulfinic acids by hydrogen bromide or of their chlorides by a mixture of trichlorosilane and tripropylamine is sometimes used to obtain symmetrical disulfides.[2] The chlorides of aromatic sulfonic acids are reduced comparatively readily to disulfides by hydrogen iodide in acetic acid. The preparation of asymmetric disulfides by the reaction of thioloesters of sulfinic acids with alkylthiotrimethylsilanes has been described.[52]

$$RS(O)SR + R^1SSiMe_3 \xrightarrow[-RSOSiMe_3]{} RSSR^1$$

5. Other methods of synthesis of disulfides

Asymmetric disulfides are frequently obtained by the thiol–disulfide exchange reaction.[2] For example, treatment of thiols with an excess of dimethyl disulfide in the presence of triethylamine leads to the formation of the corresponding alkyl methyl disulfides.

$$RSH + MeSSMe \xrightarrow{Et_3N} MeSSR + MeSH$$

The reaction of silyl sulfides with disulfides involves the exchange of the RS groups and the formation of asymmetric disulfides.[52]

$$RSSiMe_3 + R^1SSR^1 \rightleftharpoons R^1SSiMe_3 + R^1SSR$$

Asymmetric disulfides have also been obtained by treating alkyl disulfide anions, generated electrochemically from thiolate ions, with haloalkanes.[54]

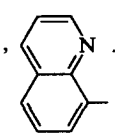
$$ArSS^- + RX \longrightarrow ArSSR$$

Ar = Ph, 2-$NO_2C_6H_4$, 4-$NO_2C_6H_4$; R = Alk.

It has been noted[54] that alkoxy- and acetoxy-disulfides are formed as a result of the ring opening and dimerisation of thiiranes in alcohols and acetic acid in the presence of germanium salts.

The monodesulfurisation of trisulfides by treatment with phosphines is sometimes used in the synthesis of symmetrical disulfides.[2] Depending on the nature of the phosphine, this entails either the removal of the terminal or the central sulfur atom. Thus, when tris(dimethylamino)phosphine is used, the terminal sulfur atom is mainly removed, whereas triphenylphosphine displaces the central sulfur atom. In order to retain the configuration in the conversion of sporidesmin trisulfide into the corresponding disulfide, triphenylphosphine is therefore employed. Disulfides are also formed in the interaction of sodium thiolates with chlorodiphenylmethane in an alcoholic medium.[55]

$$RSNa + Ph_2CHCl \xrightarrow[-NaCl]{O_2} RSSR + Ph_2C{=}O$$

R = 2,4-$(NO_2)_2C_6H_3$, .

IV. Reactions with participation of disulfides

All the reactions with participation of disulfides can be divided into three large groups: (1) reactions occurring with cleavage of the S–S bond; (2) reactions occurring with cleavage of a C–S bond; (3) reactions leading to an increase in the valence of sulfur.

1. Reactions occurring with cleavage of the S–S bond

a. Cleavage by nucleophiles

The cleavage of the S–S bond in disulfides by nucleophiles proceeds via a S_N2 mechanism.[2]

$$RSSR + Nu^- \longrightarrow \left[RS{-}\underset{\displaystyle Nu}{\overset{|}{S}}R\right]^- \longrightarrow NuSR + RS^-$$

In the absence of steric influences, the sequence based on the relative S-nucleophilicities (thiophilicities) for reactions with aryl disulfides is as follows: $P(EtO)_3 > R^-$, HS^-, $EtS^- > PhS^- > PPh_3$, $CN^- > SO_3^{2-} > OH^- > 2,4\text{-}(NO_2)_2C_6H_3S^- > N_3^- > SCN^-$, I^-, $PhNH_2$. This sequence is not identical with that based on the relative C-nucleophilicities and depends to a much greater extent on the polarisability of the nucleophile.[2]

Cleavage by C-nucleophiles. The cleavage of disulfides by C-nucleophiles has been thoroughly investigated for reactions with the cyanide anion and carbanions generated by various methods.

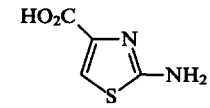
The rate of cleavage of disulfides by the cyanide anion as well as the composition and structure of the reaction products are determined primarily by the nature of the initial disulfide. For example, simple dialkyl disulfides do not react with the cyanide anion, while diphenyl disulfide does react with it and forms an equilibrium mixture of products.

$$PhSSPh + CN^- \rightleftharpoons PhSCN + PhS^-$$

The interaction of the cyanide anion with cystine results in the formation of 2-aminothiazoline-4-carboxylic acid.[2]

$$\left(HO_2CCHCH_2S{-}\right)_2 + CN^- \longrightarrow$$

$$\longrightarrow NCSCH_2CHCO_2H + {}^-SCH_2CHCO_2H$$



On treatment with the cyanide anion, tetramethylthiuram disulfide undergoes monodesulfurisation,[3] which proceeds via a S–S bond cleavage stage.

$$Me_2NCSSCNMe_2 + CN^- \longrightarrow Me_2NCS^- + Me_2NCSCN \longrightarrow$$

$$\longrightarrow Me_2NCSCNMe_2 + SCN^-$$

The cleavage of asymmetric disulfides by the cyanide anion proceeds relatively smoothly.[3]

$$ArSSR + CN^- \longrightarrow RSCN + ArS^-$$

Ar = 2-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$; R = Alk.

The rate of cleavage then depends directly on ΔpK_a—the difference between the pK_a for the thiols the residues of which form part of the disulfide molecule. The cleavage of disulfides with ΔpK_a = 1.8 proceeds in one direction. Disulfides with ΔpK_a = 1.65 to 1.05 can be attacked by the cyanide ion at both sulfur atoms. Disulfides with ΔpK_a = 0, i.e. symmetrical disulfides, do not react with the cyanide anion.[56]

The composition and nature of the products of the cleavage of asymmetric disulfides by the cyanide ion are also determined by thermodynamic factors, i.e. the cleavage takes place with formation of the thermodynamically more stable thiolate anion. The electronic factor (the cyanide anion attacks the sulfur atom with a lower electron density) and steric factors can also play a significant role.

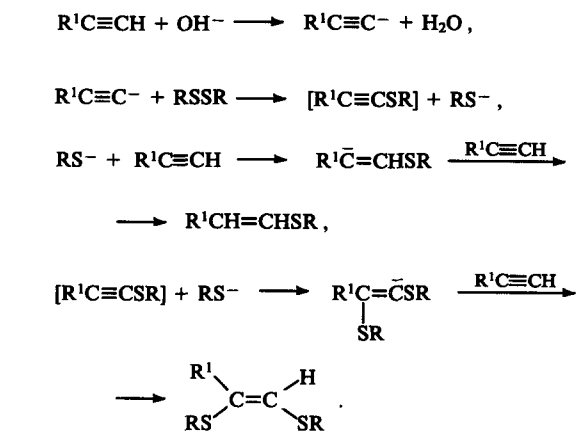
In the presence of strong bases (KOH, Bu^tOK), dialkyl disulfides react with acetylene and its homologues to form mono- and di-(alkylthio)ethenes.[57,58]

$$RSSR + R^1C{\equiv}CH \xrightarrow[H_2O\ (or\ DMSO)]{ROH\ (or\ Bu^tOK)}$$

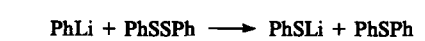
$$\longrightarrow RSC(R^1){=}CHSR + RSCH{=}CHR^1$$

R = Et, Pr^n, Bu^n; R^1 = H, Pr^n, Bu^n, Bu^t, Ph.

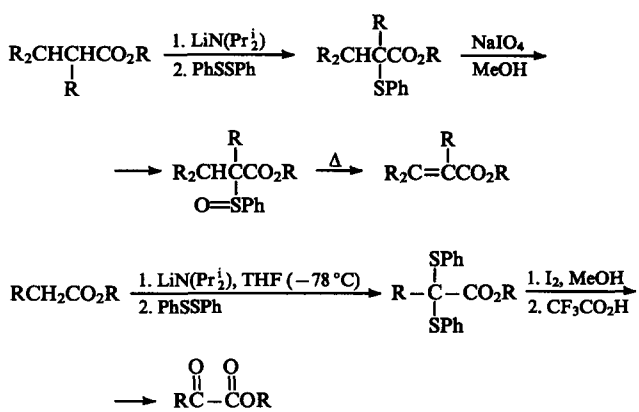
The mechanism of this reaction includes a stage in which the S–S bond is cleaved by the acetylide anion.



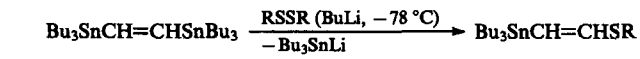
The cleavage of the S–S bond in disulfides by organolithium compounds[27] leads to thiolates and sulfides as in the case of organomagnesium compounds.[29]



The carbanions generated by treatment with Pr^i_2NLi also cleave the S–S bond in disulfides. This is one of the procedures most widely used in fine organic synthesis for the introduction of the sulfide functional group. It is used, for example, in the syntheses of α,β-unsaturated carbonyl compounds and α-oxo-esters.[59,60]

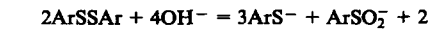


The nucleophilic substitution of the tributylstannate group by the thiolate anion obtained from disulfides by treatment with butyllithium has been described.[61]



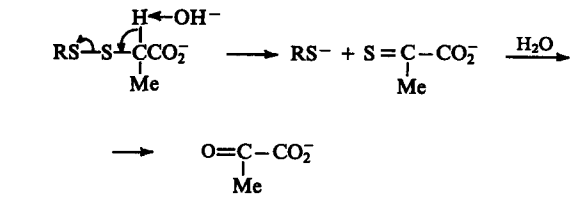
The addition of disulfides to the double bonds of cyclopentadiene in the presence of sodium hydride[62] also evidently proceeds via a stage involving the cleavage of the S–S bond by the carbanion.

Cleavage by O-nucleophiles. The reaction of disulfides with OH^- ions can proceed via one of three mechanisms depending on the structure of the initial disulfide.[2] In the absence of active α- or β-hydrogen atoms in the disulfide molecule, nucleophilic substitution takes place at a sulfur atom with formation of a thiolate anion and a sulfenic acid,[63] which disproportionates to the sulfinic acid.



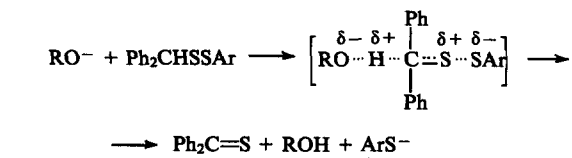
In the case of asymmetric disulfides, the hydroxide ion attacks the sulfur atom furthest from the electron-accepting group and the cleavage proceeds more readily the more stable the anion split off.

In the presence of an acid α-hydrogen atom, there is a possibility of a 1,2-elimination reaction with the initial formation of a thione, which hydrolyses to a ketone or isomerises to an enethiol.[2]

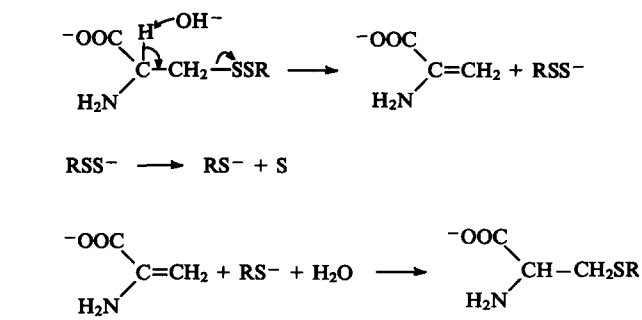


R = $CHMeCO_2^-$.

The cleavage of aryl diphenylmethyl disulfides on treatment with an alkoxide anion proceeds similarly.[2]

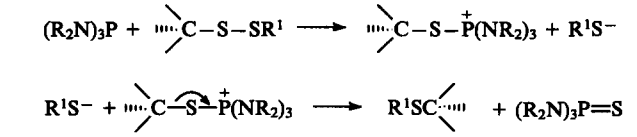


In the presence of an acid β-hydrogen atom, 1,2-elimination results in the formation of an alkene and a hydrodisulfide anion, which is converted into a thiolate anion and further into a sulfide.[2]



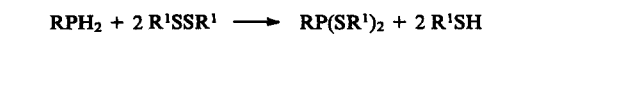
R = $CH_2CH(NH_2)COO^-$.

Cleavage by P-nucleophiles. The composition and structure of the products of the cleavage of disulfides by phosphorus compounds are determined by the nature of the organophosphorus compounds. Thus the cleavage of disulfides in the presence of dialkylaminophosphines proceeds with formation of sulfides and *N,N*-dialkylphosphoramidothioates.[27] The reaction takes place stereospecifically with inversion at one of the α-carbon atoms.



Symmetrical diallyl disulfides are more reactive than dialkyl disulfides, while asymmetric disulfides react even at room temperature.

Primary and secondary phosphines convert disulfides into thiols.[3]

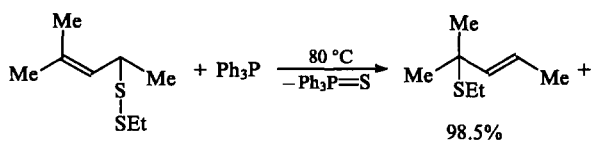


Triphenylphosphine in aqueous dioxane reduces disulfides to thiols;[64] triphenylphosphine oxide is formed simultaneously owing to the hydrolysis of the cation formed in the first stage of the reaction. In the absence of a solvent, a monosulfide and triphenylphosphine sulfide are formed.[3]

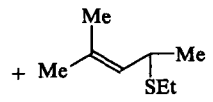
$$RSSR + Ph_3P \longrightarrow RSR + Ph_3P{=}S$$

R = $CH_2{=}CHCH_2$, $MeCH{=}CHCH_2$, $Me_2C{=}CHCH_2$ etc.

When dialkenyl and alkenyl alkyl sulfides are heated with triphenylphosphine, a mixture of two sulfides and triphenylphosphine sulfide is formed.[65]

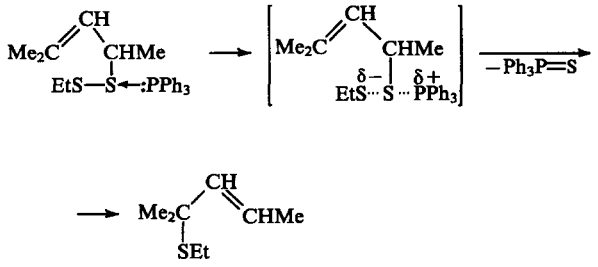


98.5%

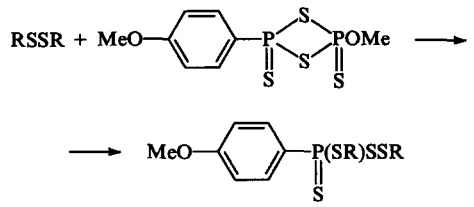


1.5%

The authors[65] believe that the reaction proceeds via an intermediate polarised complex formed as a result of the nucleophilic attack by triphenylphosphine at one of the sulfur atoms, further cleavage occurring via a S_Ni mechanism with migration of the double bond.



It has been noted[66] that the interaction of disulfides with dithiadiphosphetanes in anhydrous toluene at 120–130 °C proceeds with formation of phosphonotrithioates.



Cleavage by S-nucleophiles. The cleavage of disulfides by the thiolate anion — the thiol–disulfide exchange reaction — plays a very important role in biological processes. For example, it has been suggested[3] that the permeation of a bacteriophage through the wall of the rectum in animal organisms occurs as a result of the cleavage of the S–S bond by the thiolate anion. Asymmetric disulfides are cleaved more readily by the thiolate anion than symmetrical ones. In this case, the thermodynamic factor, i.e. the thermodynamic stability of the newly formed thiolate anion, plays an important role. The steric factor is likewise important. For example, the cleavage of di(*tert*-butyl) disulfide is approximately 10^6 times slower than that of di(n-butyl) disulfide, which is evidence in support of a S_N2 mechanism of this reaction. 1,2-Dithiolanes exhibit an anomalously high reactivity in their reaction with the thiolate anion, which has been explained[3] by the removal of the torsional strain as a result of ring opening.



The behaviour of lipoic acid in biological systems has also been explained by a similar anomalous reactivity.

Cleavage by N-nucleophiles. The cleavage of the S–S bond in bis(dialkoxyphosphonyl) and bis(dialkoxythiophosphonyl) disulfides in the presence of amines leads to sulfenamides.[67]

$$RSSR + 2\,R^1R^2NH \longrightarrow RSNR^1R^2 + RS^- + R^1R^2\overset{+}{N}H_2$$

R = CN, $(AlkO)_2P(S)$, $(AlkO)_2P(O)$.

$R^1 = R^2 = Me, H$.

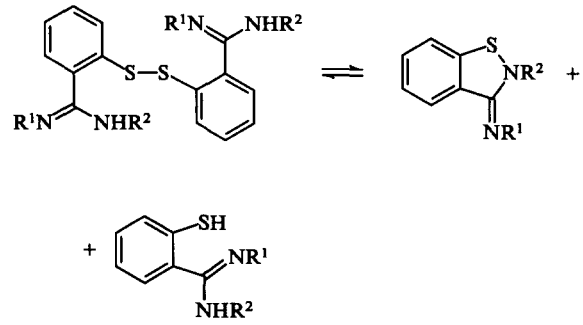
The reactivity of amines in this reaction diminishes in accordance with their basicity in the following sequence: $Me_2NH > MeNH_2 > NMe_3 > NH_3$.

The cleavage of diaryl disulfides by *N*-arenesulfonylsulfilimines in chlorobenzene leads to the formation of *N,N*-bis(arylthio)arenesulfonamides.[68]

$$ArSSAr + Ph_2S{=}NR \xrightarrow[PhCl]{\Delta} (ArS)_2NR + Ph_2S$$

Ar = 4-MeC_6H_4, Ph; R = Ts, $PhSO_2$.

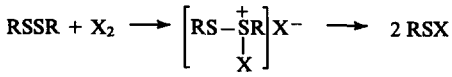
Diaryl disulfides containing amidine groups in the *ortho*-position are cleaved at the S–S bond on heating, with participation of the more nucleophilic nitrogen atom of the amidine group.[69]



$R^1 = R^2 = H$, Alk, Ar.

b. Cleavage of the S–S bond by electrophiles

The cleavage of the S–S bond in disulfides by the halogens and halogenating agents has long been known and has been thoroughly investigated. A series of preparative methods of synthesis of sulfenyl halides have been developed on the basis of this reaction.[70–72] The reaction proceeds with formation of chlorosulfonium intermediates, the cleavage of which leads to two



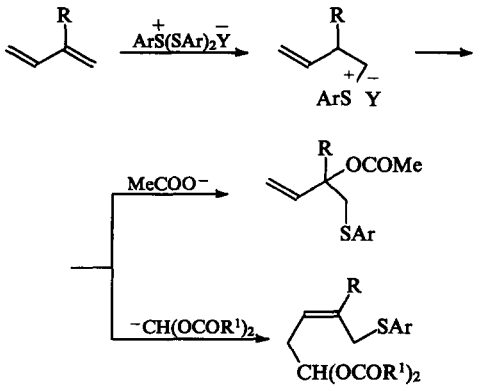
molecules of a sulfenyl halide.[70]

The interaction of disulfides with sulfenyl halides can proceed in different ways depending on the conditions. In the absence of catalysts, the reaction between diaryl disulfides and arenesulfenyl chlorides takes place with cleavage of the S–S bond and the exchange of arenesulfenyl groups.[2]

$$ArSSAr^1 + ArSX \longrightarrow \left[ArS-\overset{+}{\underset{Ar}{S}}-SAr^1\right]X^- \longrightarrow$$

$$\longrightarrow ArSSAr + Ar^1SX$$

In the presence of Lewis acids, diaryl disulfides and arenesulfenyl halides form the complexes $ArS^+(SAr)_2Y^-$ ($Y = SbCl_6$, $SbCl_4$, SbF_6, BF_4), which are effective agents for the transfer of the arylthio-cation in reactions with alkenes.[73-75]

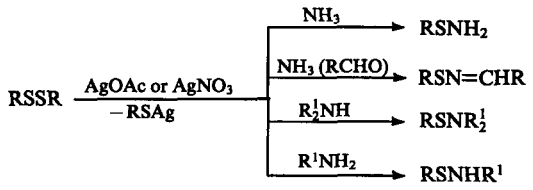


R = H, Me; R^1 = Me, Et;

Ar = Ph, 4-ClC_6H_4, 4-MeC_6H_4, C_6F_5;

Y = BF_4, SbF_6, $SbCl_6$.

In the syntheses of various sulfenamides from disulfides, the joint action of electrophiles and nucleophiles (for example Ag^+ ions and amines) is used to cleave the S–S bond.[2,76,77]



R = 4-MeC_6H_4, 3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$ etc.;

R^1 = Me, Et, Pr^i, Bu, etc.

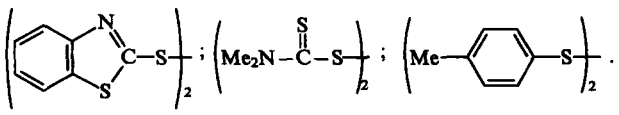
It has been noted[78] that, on heating in acetic anhydride, diphenyl disulfide is cleaved, affording the following products: PhSH, PhSAc, and $(PhS)_3CMe$.

c. Homolytic cleavage of the S–S bond

Many disulfides exhibit thermochromism (they are reversibly coloured on heating). In order to account for this phenomenon, the erroneous hypothesis has been put forward that the thermochromism is due to the reversible dissociation of disulfides into thiyl radicals, which are present at an appreciable concentration.

$$RSSR \rightleftarrows 2RS^\cdot$$

When disulfides are heated, the homolysis of the S–S bond does indeed take place but with very low rate constants (k), which have the following values at 100 °C:[2]



$k = 8.3 \times 10^{-5}\ s^{-1}$ $k = 5.5 \times 10^{-6}\ s^{-1}$ $k \leqslant 2 \times 10^{-8}\ s^{-1}$

The pyrolysis of dialkyl disulfides in the gas phase begins at 200 °C. The thermal decomposition temperature is then reduced with increase in the length of the alkyl groups and the degree of their branching.[79] The pyrolysis of dimethyl disulfide in the gas phase at 316–317 °C under reduced pressure (3.2 to 3.0 kPa) takes place with formation of hydrogen sulfide, ethylene, sulfur, and other products. It has been suggested[27] that the pyrolysis begins with the homolytic cleavage of the S–S and C–S bonds; the radicals MeS$^\cdot$ and atomic sulfur, formed under these conditions, react subsequently with the initial disulfide. (In a high vacuum, dimethyl disulfide dissociates into thioformaldehyde and methanethiol.)

$$MeSSMe \longrightarrow CH_2{=}S + MeSH$$

Judging from the nature of the final products, the pulsed vacuum pyrolysis of diisopropyl disulfide at 500 °C begins with the homolytic rupture of a C–S bond accompanied by the formation of isopropyldisulfane as an intermediate, which subsequently decomposes into propene, hydrogen sulfide, and sulfur.[80]

$$Me_2CHSSCHMe_2 \longrightarrow [Me_2CHSSH] \longrightarrow$$

$$\longrightarrow MeCH{=}CH_2 + HSSH$$

$$HSSH \longrightarrow H_2S + S$$

The pyrolysis of di(*tert*-butyl) disulfide also begins with the homolysis of a C–S bond and is completed by the formation of H_2S, CS_2, CH_4, and $CH{\equiv}CH$.[27,79] Hence, on passing from dimethyl disulfide to diisopropyl and di(*tert*-butyl) disulfides, the probability of the cleavage of a C–S bond increases owing to the decrease in the dissociation energy of this bond in the above series.

The vacuum pyrolysis of diphenyl and di(naphth-2-yl) disulfides at 400–700 °C takes place with formation of thiyl radicals owing to the homolytic cleavage of the S–S bond.[27]

The thiyl radicals obtained by the pyrolysis of disulfides are used in organic synthesis as highly reactive intermediates. For example, the thiyl radicals generated from the diphenyl disulfide in the liquid phase at 125–230 °C react with bromoarenes in hydrogen sulfide to form the corresponding asymmetric sulfides.[81]

$$2\,ArBr + Ph_2S_2 \xrightarrow{H_2S} 2\,ArSPh + 2\,HBr$$

$$PhSSPh \xrightarrow{\Delta} 2\,PhS^\cdot$$

$$ArBr \longrightarrow Ar^\cdot + Br^\cdot$$

$$PhS^\cdot + H_2S \longrightarrow PhSH + HS^\cdot$$

$$Br^\cdot + H_2S \longrightarrow HBr + HS^\cdot$$

$$Ar^\cdot + H_2S \longrightarrow ArH + HS^\cdot$$

$$PhSH + Br^\cdot \longrightarrow PhS^\cdot + HBr$$

$$PhSH + Ar^\cdot \longrightarrow PhS^\cdot + ArH$$

$$ArBr + PhS^\cdot \longrightarrow \left[R\text{–}\langle\rangle\text{(SPh, Br)}\right] \xrightarrow[-HBr]{PhSH}$$

$$\longrightarrow ArSPh + PhS^\cdot$$

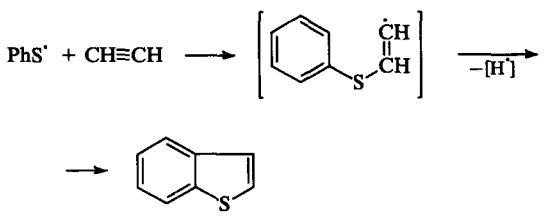
The radicals PhS$^\cdot$ play also the role of agents transferring hydrogen atoms from H_2S to the Br$^\cdot$ and Ar$^\cdot$ radicals in this reaction. The temperature of the thiylation of bromoarenes in

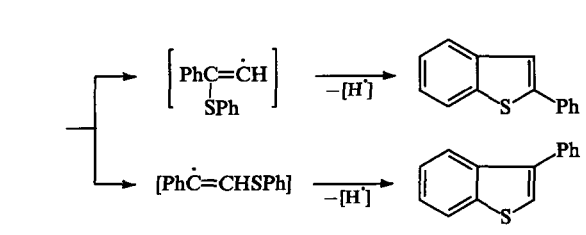
accordance with this scheme decreases after the introduction of a π-dative substituent into the benzene ring. Chloro-derivatives of benzene, thiophene, and naphthalene react with disulfides at higher temperatures than the bromo-derivatives owing to the greater resistance of the C–Cl bond to thermal homolysis.[82–84]

$$RSSR + R^1Cl \xrightarrow{600-630\ ^\circ C} RSR^1 + RSCl$$

R = Alk; R^1 = Ph, 4-MeC_6H_4, $C_{10}H_7$, C_4H_3S, 2-ClC_6H_4, 4-$CF_3C_6H_4$, 3,4-$Cl_2C_6H_3$.

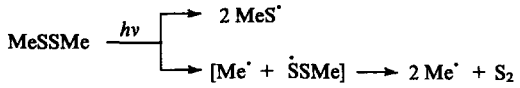
The thiyl radicals generated by the thermolysis of diphenyl disulfide at 550 °C react with acetylene and phenylethyne to form benzo[*b*]thiophene and 2- and 3-phenylbenzo[*b*]thiophenes respectively.[85]





At higher temperatures, the addition of the phenylthiyl radical to phenylethyne and other acetylene homologues leads to phenyl vinyl sulfides.[86,87]

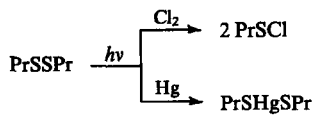
Depending on the wavelength of the radiation, the gas-phase photolysis of disulfides can proceed with homolytic cleavage of both the S–S and C–S bonds.[27] Thus, on irradiation of dimethyl disulfide with UV light at a wavelength < 195 nm, the ratio of the products formed as a result of the homolysis of the C–S and S–S bonds is 1.35 : 1.



When sources of radiation with a wavelength of 254 nm are used, the photolysis of the C–S bond becomes insignificant provided that the alkyl radical is not stabilised by the corresponding functional groups. The main process in this case becomes the homolysis of the S–S bond with formation of thiyl radicals. In the case of primary and secondary dialkyl disulfides, these radicals readily recombine in solution; this is used in the synthesis of asymmetric dialkyl disulfides.

$$RSSR + R^1SSR^1 \overset{h\nu}{\rightleftharpoons} 2\,RSSR^1$$

The equilibrium position is determined by the nature of the alkyl group. In the case of alkyl groups having the normal structure, the ratios RSSR : $RSSR^1$: R^1SSR^1 are 1 : 2 : 1.[27] The photochemical homolysis of the S–S bond in disulfides in the presence of chlorine or elemental mercury leads respectively to sulfenyl chlorides and mercury thiolates.[27]



The thiyl radicals generated in the photolysis of diaryl disulfides enter into the homolytic chlorine substitution reaction in trichloro- and tetrachloroethenes, affording $ArSCH=CCl_2$, $ArSCCl=CHCl$, and $ArSCCl=CCl_2$.[88] In liquid ammonia, on UV irradiation in a quartz bulb for 12 h diaryl disulfides react with trifluoromethyl iodide, forming the corresponding aryl trifluoromethyl sulfides.[89]

$$XC_6H_4S-SC_6H_4X \xrightarrow{2\,CF_3I\,(h\nu)} 2\,XC_6H_4SCF_3$$

X = H, 4-Cl, 2-NO_2, 4-NO_2.

After prolonged irradiation of diphenyl disulfide and its *para*-chloro-derivative, a series of side products are formed, so that the yields of the corresponding sulfides are 12% and 36% respectively. The presence of the nitro-group hinders the radical side processes and the yields of *p*- and *o*-nitrophenyl trifluoromethyl sulfides reach 58% and 72%.

The homolytic cleavage of the S–S bond in disulfides also takes place in the presence of free radicals and compounds which are sources of free radicals (peroxides, diazo-compounds, azo-compounds, etc.). The homolytic cleavage of the S–S bond in disulfides by free radicals constitutes the basis of the polymer chain transfer process in radical polymerisation.[6]

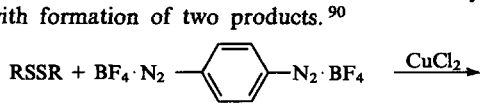
The aryl radicals formed as a result of the cleavage of diazonium salts afford sulfides on reaction with symmetrical disulfides.[90]

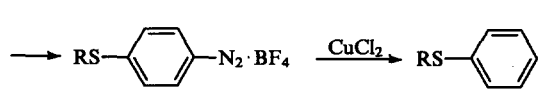
$$4\text{-}ClC_6H_4N_2X \xrightarrow[-N_2,\ -X^-]{CuCl_2} 4\text{-}ClC_6H_4^{\bullet}$$

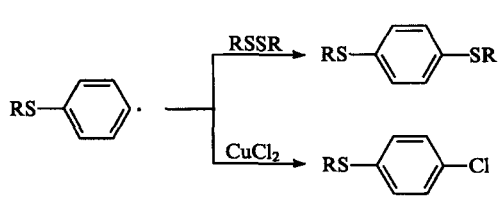
$$4\text{-}ClC_6H_4^{\bullet} + RSSR \longrightarrow 4\text{-}ClC_6H_4SR + RS^{\bullet}$$

R = Bu, $PhCH_2$, Ph; X = Cl, BF_4.

Benzenebisdiazonium tetrafluoroborates arylate disulfides with formation of two products.[90]







R = Bu, Ph, $PhCH_2$.

d. Reduction of disulfides

The reduction of disulfides takes place with cleavage of the S–S bond and the formation of thiols.

$$RSSR \xrightarrow{Red} 2\,RSH$$

A series of preparative methods of synthesis of thiols, described in the scientific literature and in handbooks, have been developed on the basis of this reaction. Zinc in acetic, hydrochloric, and sulfuric acids,[70] metallic sodium in xylene,[70] sodium hydrogen sulfide in alcohol,[29] lithium tetrahydroaluminate in ether or tetrahydrofuran,[91] and the $BF_3 \cdot H_2O - Et_3SiH$ system[92] are used as the reductants. Bis(trifluoromethyl) disulfide is relatively easily reduced in the presence of powdered activated copper in dimethylformamide[89] or acetonitrile.[93]

$$CF_3SSCF_3 \xrightarrow{2\,Cu\ (DMF\ or\ MeCN)} 2\,CF_3SCu \cdot DMF(MeCN)$$

In dimethylformamide, the reaction is exothermic and is completed after 1 h, whereas in acetonitrile the reduction takes place over a period of 14–16 h. The ease of the cleavage of the S–S bond in bis(trifluoromethyl) disulfide in the presence of copper has been explained[93] by the high oxidising capacity of this compound.

The traditional method for the reduction of disulfide bonds in proteins involves the treatment of the protein with a large excess of a thiol. The thiol–disulfide exchange reaction then takes place.[2]

$$RSSR + 2\,R^1SH \rightleftharpoons 2\,RSH + R^1SSR^1$$

Dithiothreitol $HSCH_2CH(OH)CH(OH)CH_2SH$ is used nowadays for such purposes. The reduction of cystine to cysteine in living organisms takes place mainly as a result of the action of the enzyme glutathionecystine-oxidoreductase.[2]

e. Insertion of sulfur and other reagents in the S–S bond

Certain cyclic sulfides and disulfides are converted into trisulfides on interaction with a dihydrodisulfide. It has been suggested[2] that the reaction proceeds via the insertion of sulfur in the S–S bond and not via nucleophilic substitution at a carbon atom.

$$RSSR \xrightarrow{HSSH} \left[RS-\overset{S}{\overset{\|}{S}}R\right] \longrightarrow RSSSR$$

This hypothesis has been confirmed to some extent by the fact that the conversion of sporidesmin (S_2 bridge) into sporidesmin E (S_3 bridge) in the presence of dihydrodisulfide takes place with retention of configuration.

The insertion of carbenes in the S–S bond of disulfides leads to the formation of thioacetals.[94]

$$RSSR + :CH_2 \longrightarrow RSCH_2SR$$

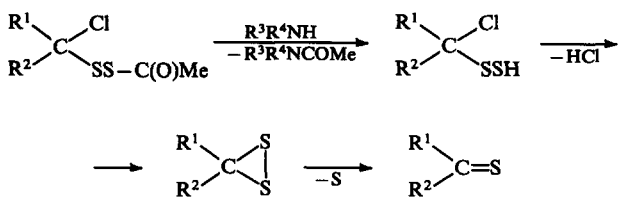
2. Reactions involving the cleavage of a C–S bond

The cleavage of a C–S bond is less characteristic of disulfides than the cleavage of the S–S bond. The cleavage of the S–S bond is sometimes accompanied by the cleavage of a C–S bond, which has already been noted in the case of the photolysis or the thermolysis of disulfides.

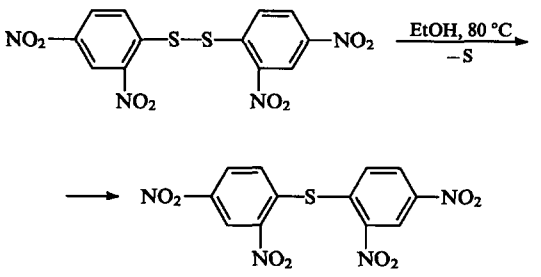
Disulfides containing readily removable groups at the sulfur atom, such as RCO, $PhCH_2$, $HOOCCH_2$, $2,4\text{-}(NO_2)_2C_6H_3$, etc. show the greatest tendency towards the cleavage of a C–S bond. For example, when a diacyl disulfide is acted upon by chlorine, the S–S bond and not a C–S bond is cleaved with formation of acyldisulfenyl chlorides.[72]

$$RC(O)SSC(O)R \xrightarrow{Cl_2} RC(O)SSCl + RC(O)Cl$$

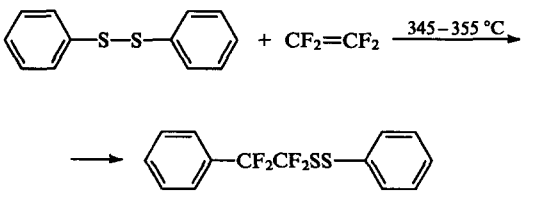
A C–S bond in acetyl α-chloroalkyl disulfides is cleaved by secondary amines with formation of α-chloroalkyl disulfones, which are converted into unstable cyclic disulfides as a result of the elimination of hydrogen chloride.[95]



On heating in alcohol, bis(2,4-dinitrophenyl) disulfide is readily converted into the corresponding sulfide, as a result of the cleavage of the C–S and S–S bonds.[96]



The thermal insertion of tetrafluoroethene in a C–S bond of diphenyl disulfide with formation of phenyl β-phenyltetrafluoroethyl disulfide has been described.[97]



40%

The cleavage of a C–S bond also occurs in various rearrangements of disulfides. Thus diallyl disulfide and its substituted derivatives rearrange to the thioanion $CH_2{=}CHCH_2.SCH_2CH{=}CHS^-$ on treatment with the dimethyl sulfoxide (DMSO)–MOH (M = K, Na) superbasic system.[98] Under the same conditions, the disulfides $RSSCHCH{=}CH_2$ (R = Et, Pr) rearrange to the corresponding thioanions, the subsequent alkylation of which by alkyl iodides leads to the bissulfides $RSCH_2CH{=}CHSR^1$ (R^1 = Pr, Pr^i). The alkylation of diallyl disulfides by alkyl halides in the DMSO–NaOH(KOH) superbasic system leads to 1-alkylthio-3-allylthio-1-propenes and 1,3-di(alkylthio)-1-propenes.[99]

$$CH_2{=}CHCH_2SSCH_2CH{=}CH_2 \xrightarrow{RX\ (MOH/DMSO)}$$

$$\longrightarrow RSCH{=}CHCH_2SCH_2CH{=}CH_2$$

$$\longrightarrow RSCH{=}CHCH_2SR$$

Under similar conditions, 1-alkylthiobuta-2,3-dienes rearrange to 2-alkylthio- and 1-alkylthio-buta-1,3-dienes.[99]

3. Reactions involving an increase in the valence of sulfur

a. The formation of sulfonium complexes

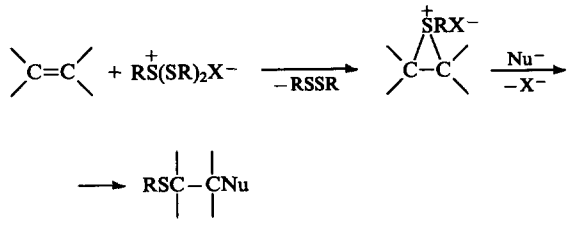
As already mentioned, the interaction of disulfides with sulfenyl halides in the presence of Lewis acids leads to the formation of sulfonium complexes in which the sulfonium cation is stabilised by the anionoid fragment of the Lewis acid.[27,73–75]

$$RSSR + RSCl + SbCl_5 \longrightarrow R\overset{+}{S}(SR)_2SbCl_6^-$$

Complexes of a similar structure are also formed in the interaction of disulfides with the alkyl esters of trifluoromethanesulfonic acid.[100]

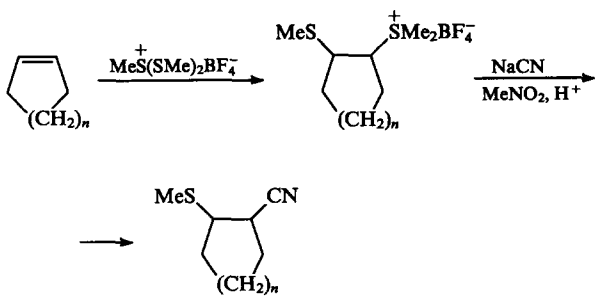
$$(MeS)_2 + CF_3SO_3Me \xrightarrow{CH_2Cl_2,\ 0\,^\circ C,\ N_2} Me\overset{+}{S}(SMe)_2CF_3SO_3^- \quad 84\%$$

Such complexes have found applications in organic synthesis as RS^+ group transfer agents. The interaction of sulfonium complexes with alkenes can proceed differently. In some cases, the reaction involves the formation of episulfonium ions, which undergo ring opening on treatment with nucleophiles, giving rise to sulfides.[100-102]



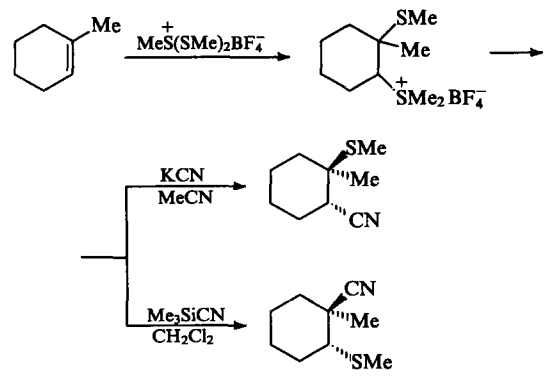
R = Alk, Ar; X = CF_3SO_2, $SbCl_6$, BF_4, etc.

In other cases, for example in the addition of sulfonium complexes to cycloalkenes, adducts are formed, their behaviour in reactions with nucleophiles being similar to that of episulfonium salts. A general mild cyanosulfenylation method has been developed on the basis of this reaction.[27]

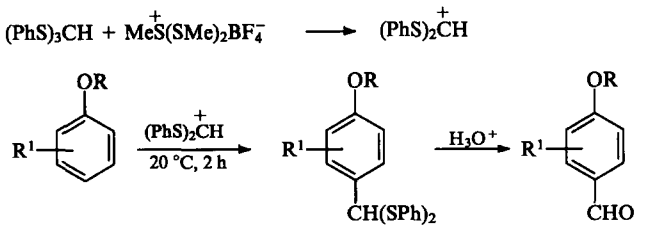


n = 1, 2.

Depending on the conditions in the reaction with nucleophiles, both regioisomers may be obtained.[27]



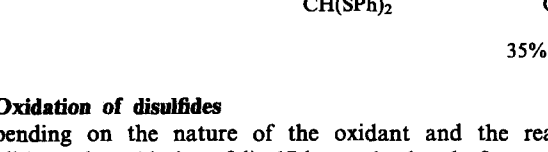
A method for the regioselective formylation of phenols and naphthols has been developed using sulfonium complexes and thioacetals.[103]



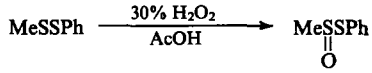
35%-87%

b. Oxidation of disulfides

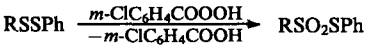
Depending on the nature of the oxidant and the reaction conditions, the oxidation of disulfides can lead to the formation of thiolosulfinates, thiolosulfonates, disulfones, and sulfonic acids.



Symmetrical thiolosulfinates are formed as a result of the oxidation of symmetrical disulfides by peroxyacids, sodium metaperiodate, and ammonium persulfate or by photosensitised oxidation in the presence of Methylene Blue.[70] Asymmetric thiolosulfinates are formed in the oxidation of asymmetric disulfides by 30% hydrogen peroxide in acetic acid.[104] The oxidation then proceeds regioselectively at the more nucleophilic sulfur atom.



The use of an excess of hydrogen peroxide leads to thiolosulfonates, which are also formed in the oxidation of disulfides by cold nitric acid and vanadium pentoxide[70] or by chlorine in acetic acid with subsequent hydrolysis.[105] The oxidation of asymmetric disulfides by *m*-chloroperbenzoic acid also takes place regioselectively at the more nucleophilic sulfur atom.[106]



The oxidation of disulfides RSSR (R = Me, Bu, Ph, $PhCH_2$) by the $H_2O_2-Na_2WO_4$ system in the presence of acetyltrimethylammonium chloride leads to the formation of the disulfones RSO_2SO_2R in 46%-81% yield.[107]

Disulfides are oxidised by hot nitric, chromic, and performic acids or potassium permanganate to sulfonic acids.[2] The reaction of disulfides with the radical-anion $^-O-O^-$, generated from KO_2 and anhydrous 18-crown 6-ether in dry pyridine at 25 °C, leads to the formation of a mixture of RSO_2^- and RSO_3^-.[108]

The standard method for the cleavage of disulfide bonds in proteins involves treatment of the latter with performic acid. The cysteine and cystine residues are then converted after hydrolysis[2] into cysteic acid $HO_2CCH(NH_2)CH_2SO_3H$. Chlorination of disulfides by chlorine in acetic acid leads to the formation of the chlorides of sulfinic[109] or sulfonic[2] acids.

c. Oxidative imination of disulfides

The reactions accompanied by the oxidation of an element and the formation of the imino-group have come to be called oxidative imination.[110] The oxidative imination of disulfides by *N*-chloro- and *N,N*-dichloro-compounds can lead to the formation of the chlorides, amides, and esters of iminosulfinic acids.

The formation of the chlorides of iminosulfinic acids. The interaction of disulfides with *N,N*-dichloroamides or

N,N-dichloroamines in anhydrous aprotic organic solvents for a 1 : 1 reactant ratio leads to the formation of the chlorides of *N*-substituted iminosulfinic acids and sulfenyl chlorides.[112–115]

$$RSSR + R^1NCl_2 \longrightarrow RS(=NR^1)Cl + RSCl$$

R = Ph, $PhCH_2$, 4-ClC_6H_4, 4-$NO_2C_6H_4$, 2-$NO_2C_6H_4$;
R^1 = $ArSO_2$, ArCO, Bu^t, $Me_2C(CN)$, CF_3SO_2.

In the case of asymmetric disulfides, the sulfenyl chlorides formed contain more highly electron-accepting groups, since the sulfur atom with a high electron density undergoes oxidative imination. The sulfenyl chlorides formed can react further under more severe conditions with *N,N*-dichloro-compounds to form *N*-substituted chlorides of iminosulfinic acids, so that for preparative purposes the reaction is carried out in a single stage without isolating the sulfenyl chlorides. The chlorides of *N*-(benzenesulfonyl)areneiminosulfonic acids are formed in the reaction of diaryl disulfides with chlorine in acetic acid and subsequent treatment of the reaction mixture with the *N,N*-dichloroamide of benzenesulfonic acid.[116]

$$ArSSAr \xrightarrow[AcOH]{Cl_2} 2\,ArS(O)Cl \xrightarrow[-Cl_2]{2\,PhSO_2NCl_2} 2\,ArS(O)(Cl)=NSO_2Ph$$

In the reaction of disulfides with the *N*-chloroamides of carboxylic acids, the chlorides of *N*-acyliminosulfinic acids are obtained.[117]

$$ArSSAr + 3\,RCONHCl \longrightarrow 2\,ArS(=NCOR)Cl + RCONH_2 + HCl$$

The reaction takes place in stages. For a 1 : 1 reactant ratio, *N*-acylsulfenamides and sulfenyl chlorides are formed initially and then react further with the *N*-monochloroamide.

$$ArSSAr + RCONHCl \longrightarrow ArSNHCOR + ArSCl$$

$$ArSNHCOR + RCONHCl \longrightarrow ArS(=NCOR)Cl + RCONH_2$$

$$ArSCl + RCONHCl \longrightarrow ArS(=NCOR)Cl + HCl$$

The interaction of diaryl disulfides with the alkyl esters of *N*-chlorobenzenecarboxyimidic acid for a 1 : 1 reactant ratio leads similarly to the formation of the corresponding alkyl esters of *N*-(arylthio)benzenecarboxyimidic acid and arenesulfenyl chlorides. The latter react further with the *N*-chloroimino-ester, affording the chlorides of *N*-benzoylareneiminosulfinic acids.[118]

$$ArSSAr + ClN{=}C(OAlk)Ph \longrightarrow ArSN{=}C(OAlk)Ph + ArSCl$$

$$ArSCl + ClN{=}C(OAlk)Ph \longrightarrow ArS(=NCOPh)Cl + AlkCl$$

The oxidative imination of disulfides by sodiochloroamides of sulfonic acids in aqueous media leads to the amides of aminosulfinic acids.[119–121] As in the oxidation of thiols to disulfides,[122] the reactivity of the disulfides with respect to the sodiochloroamides of sulfonic acids is then directly related to the pK_a of the corresponding thiols the residues of which form the disulfides. Consequently the acid properties of thiols can be used as a quantitative criterion for the estimation of the reactivities of disulfides with respect to the sodiochloroamides of sulfonic acids. Indeed, it has been shown[121] that the disulfides for which the pK_a for the corresponding thiols are in the range 7–11 are relatively easily iminated by the sodiochloroamides of sulfonic acids. A decrease in the pK_a for the thiols to 5–6 leads to a decrease in the rate of the imination reaction and in the yield of the amides of iminosulfinic acids. The disulfides where the pK_a for the corresponding thiols are less than 5 are not iminated by the sodiochloroamides of sulfonic acids. Such disulfides contain as a rule highly electron-accepting groups at the sulfur atoms which reduce the nucleophilicity of the latter. The imination of asymmetric disulfides by the sodiochloroamides of sulfonic acids takes place regioselectively at the more nucleophilic sulfur atom.[123] From the standpoint of the acid properties of the corresponding thiols, this means that the pK_a for the thiol the residue of which is iminated is higher than that for the thiol the residue of which is eliminated. This residue gives rise to symmetrical disulfides.

$$RSSR^1 + 2\,PhSO_2NNaCl \cdot xH_2O \xrightarrow[-0.5\,R^1SSR^1,\ -2\,NaCl]{} RS(=NSO_2Ph)NHSO_2Ph$$

R = Bu; R^1 = 4-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$;
R = Ph; R^1 = 4-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$;
R = 4-MeC_6H_4; R^1 = 2,4-$(NO_2)_2C_6H_3$;
R = $PhCH_2$; R^1 = 2,4-$(NO_2)_2C_6H_3$.

The interaction of *N,N*-dichloro-compounds with sodium thiolates, which results in the formation of the sodium salts of the amides of iminosulfinic acids,[125–133] proceeds via a disulfide formation stage.

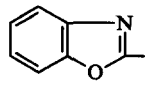
$$5\,RSNa + 2\,R^1NCl_2 \xrightarrow[-2\,RSSR,\ -2\,NaCl]{} RS(=NR^1)N(Na)R^1$$

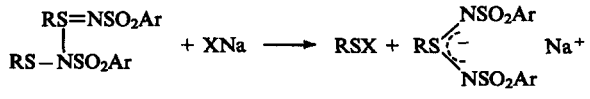
R = Alk, Ar, Het, $AlkOCOCH_2$, $ArNHCOCH_2$;
R^1 = $ArSO_2$, ArCO, $(PhO)_2P(O)$, $(NCCH_2CH_2)_2NC(O)$.

In inert solvents and in the absence of moisture, diaryl disulfides react with the sodiochloroamides of sulfonic acids, forming *N*-arylthio-*N,N'*-bis(arenesulfonyl)arenesulfinamidines,[134–136] which are also obtained on interaction of sodium thiolates with the dichloroamides of sulfonic acids for a 2 : 1 reactant ratio.[137–140] These compounds have found applications in organic synthesis as ArS^+ transfer agents in reactions with nucleophiles[138] and unsaturated compounds.[135]

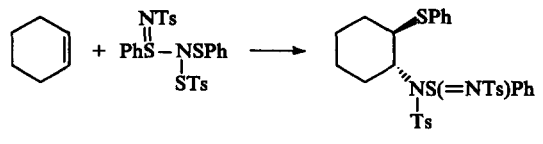
$$RSSR + 2\,ArSO_2NNaCl \xrightarrow[-NaCl]{} RS(=NSO_2Ar)N(SR)SO_2Ar$$

$$4\,RSNa + 2\,ArSO_2NCl_2 \xrightarrow[-RSSR,\ -4\,NaCl]{} RS(=NSO_2Ar)N(SR)SO_2Ar$$

R = Ph, 4-MeC_6H_4, 



X = OH, RS, RO, $ArSO_2NH$.



It is believed[124,133,138] that *N*-arylthio-*N,N'*-bis(arenesulfonyl)arenesulfinamidines are intermediates in the reactions of disulfides with the sodiochloroamides of sulfonic acids in aqueous media and also of sodium thiolates with the dichloroamides of sulfonic acids for a 5 : 2 reactant ratio. The sequence of the reactions in the imination of thiols by the sodiochloroamides of sulfonic acids is therefore as follows:

$$2\,RSH + ArSO_2NNaCl\cdot xH_2O \longrightarrow RSSR + ArSO_2NH_2 + NaCl$$

$$RSSR + 2\,ArSO_2NNaCl \longrightarrow$$

$$\longrightarrow RS(=NSO_2Ar)N(SR)SO_2Ar + 2\,NaCl$$

$$RS(=NSO_2Ar)N(SR)SO_2Ar + H_2O \longrightarrow$$

$$\longrightarrow RS(=NSO_2Ar)NHSO_2Ar + RSOH$$

$$RSOH \longrightarrow 0.2\,RSO_3H + 0.4\,RSSR + 0.4\,H_2O.$$

The introduction into the reaction of yet another mole of the sodiochloroamide of the sulfonic acid can lead to the formation of an additional amount of the iminosulfinamide, but the disulfide does not fully disappear from the reaction mixture, since it is reformed as a result of the disproportionation of the sulfenic acid. The formation of an appreciable amount of side products naturally reduces the yield of the amides of iminosulfinic acids, which does not as a rule exceed 60% in this case.

The interaction of disulfides with the *N*-chloroamides of carboxylic[117,141,142] and phosphonic acids[143] in anhydrous organic solvents (CH_2Cl_2, CCl_4) in the presence of pyridine leads to the formation of *N,N'*-disubstituted amides of iminosulfinic acids.

$$RSSR + 4\,AcNHCl + 3\,C_5H_5N \xrightarrow[-2\,C_5H_5N\cdot HCl \\ -\,C_5H_5N\cdot Cl_2]{} 2\,RS(NAc)-NHAc$$

R = Me, Bu, C_5H_{11}, C_7H_{15}, Ph, 4-MeC_6H_4, 4-$NO_2C_6H_4$;

Ac = PhCO, $(PhO)_2PO$.

In the absence of bases and for a 1 : 2 reactant ratio, diazasulfonium salts are formed. They decompose on heating with formation of *N,N'*-diacylsulfinamidines.[117]

$$ArSSAr + 2\,RCONHCl \longrightarrow Ar\overset{+}{S}(NHCOR)_2Cl^- \xrightarrow[-\,HCl]{\Delta}$$

$$\longrightarrow ArS(=NCOR)NHCOR$$

The formation of iminosulfinic acid esters. The interaction of disulfides with the sodiochloroamides of sulfonic acid in alcoholic media leads to the formation of a mixture of amides and alkyl esters of iminosulfinic acids.[144] The formation of iminosulfinic acid esters is due to the interaction, according to the authors,[144] of the intermediate chlorides of the iminosulfinic acids with alcohols.

$$RSSR + TsNNaCl \longrightarrow \left[\begin{matrix} RS=NTs \\ | \\ Cl \end{matrix}\right] \longrightarrow$$

$$\xrightarrow[-Cl^-]{TsNH^-} RS(=NTs)NHTs$$

$$\xrightarrow[-HCl]{R^1OH} RS(=NTs)OR^1$$

On the other hand, according to Levchenko,[124] the formation of iminosulfinic acid esters is caused in this case by the imination of the sulfenic acid esters formed as a result of the cleavage of *N,N'*-bis(arenesulfonyl)-*N*-(R-sulfenyl)sulfinamidines in the presence of alcohols.

$$RSSR + 2\,TsNNaCl \xrightarrow[-2NaCl]{} RS(=NTs)N(SR)Ts$$

$$RS(=NTs)N(SR)Ts + R^1OH \longrightarrow$$

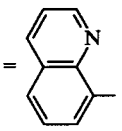
$$\longrightarrow RS(=NTs)NHTs + RSOR^1$$

$$RSOR^1 + TsNNaCl \xrightarrow[-NaCl]{} RS(=NTs)OR^1$$

The formation of the alkyl esters of iminosulfinic acids has been noted[145,146] in the reaction of disulfides with the *N,N'*-dichloroamides of sulfonic acids in the presence of alkalis in alcoholic media.

$$RSSR + 2\,PhSO_2NCl_2 + 2\,R^1OH + Na_2CO_3 \xrightarrow[-2NaCl,\,-2CO_2,\\ -Cl_2,\,-H_2O]{}$$

$$\longrightarrow 2\,RS(=NSO_2Ph)OR^1$$

R =  ; R^1 = Me, Et.

4. The applications of disulfides

a. Biological activity

Disulfides occur to a much lesser extent in many biologically active preparations than other compounds of divalent sulfur. They are used much more often as initial compounds or intermediates in the manufacture of biologically active substances.[7] However, individual representatives of disulfides exhibiting a relatively high biological activity are also encountered. For example, it has been noted[2,3] that 1-methylthiopropyl propenyl and *sec*-butyl 3-methylthioallyl disulfides, isolated from the resin of *Asa foetida*, exhibit a relatively high insecticidal activity. Glyotoxin and sporidesmin possess antifungal, antibacterial, and antiviral activities.[147]

b. The use of disulfides in polymer chemistry

Certain disulfides, in particular bis(2-benzothiazolyl) disulfides have found extensive applications as accelerators of the vulcanisation of rubbers.[5] Bis(*o*-benzamidophenyl) disulfide is used as the accelerator of the plasticisation of cured rubbers and bis(2,4-dimethylphenyl) disulfide is employed as an accelerator of the regeneration of cured rubbers.[148]

Disulfides are effective polymer chain transfer agents in radical polymerisation reactions,[6] since the thiyl radical formed as a result of chain transfer is relatively reactive and participates in the initiation of a new chain.

$$\sim CH_2\dot{C}H + RSSR \longrightarrow \sim CH_2\underset{R}{\underset{|}{C}}HSR + RS^{\cdot}$$

$$RS^{\cdot} + CH_2=CHR \longrightarrow RSCH_2\underset{R}{\underset{|}{\dot{C}}}H$$

The ability of disulfides to transfer a polymer chain is characterised by the transfer constant *C*, which is equal to the ratio of the transfer rate constant K_f to the chain propagation constant K_p:

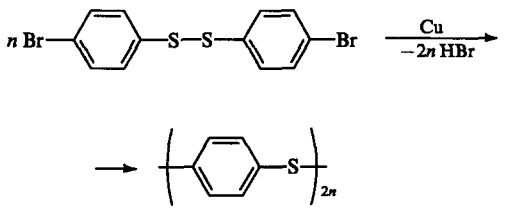
$$C = K_f / K_p$$

The higher the transfer constant, the more readily are disulfides subjected to attack by a free radical.

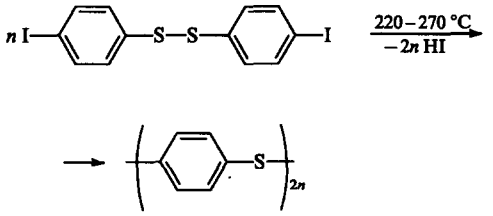
The chain transfer constants for disulfides are lower than for the corresponding peroxide compounds. For example, the chain transfer constant for dibenzoyl disulfide is five times lower than for benzoyl peroxide, which can be explained, on the one hand, by the smaller strength of the O–O bond in peroxides compared with that of the S–S bond in disulfides and, on the other, by a different chain transfer mechanism in the case of peroxide compounds. The main reaction for disulfides is the cleavage of the S–S bond by the macroradical, while for peroxide compounds it is the abstraction of a hydrogen atom.

It has been noted [149] that bis(glycylaminophenyl) disulfides are iniferters, which make it possible to obtain hydrophobic [poly(methylmethacrylate), polystyrene] and hydrophilic (poly-*N*-methylmethacrylamide) macroinitiators with a wide set of molecular masses, which can be used for the synthesis of block-copolymers of the A–B–A type.

The synthesis of poly(1,4-phenylene sulfide) in which bis-(4-bromophenyl) disulfide is used as a monomer has been described. [150]



The synthesis is carried out in a boiling mixture of quinoline and pyridine in the presence of equimolecular amounts of copper powder. The reaction takes place over a period of 8 h with formation of poly(phenylene sulfide) with a molecular mass $\leqslant 4000$ and in 76% yield. The synthesis of poly(1,4-phenylene sulfide) by the thermolysis of bis(4-iodophenylene) disulfide has been described. [151]



The thermolysis is carried out at 220–270 °C in diphenyl ether. The polymer formed has a molecular mass of 20 000 and a high mechanical strength and thermal stability.

* * *

Thus the studies in the chemistry of disulfides during the last 10–15 years have been largely directed to further development of the methods of synthesis of disulfides already known and to the search for new ones (syntheses based on alkylthiotrimethylsilanes, thiocyanates, sulfenyl thiocyanates, etc.). Much attention has been devoted to the study of the reactivity of disulfides and in particular of reactions occurring with formation of sulfonium complexes and imino-compounds of tetravalent sulfur. The previous studies on the use of disulfides in polymer chemistry underwent further development in recent years.

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