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Sulfides: synthesis and properties

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Abstract. The review gives a systematic account and surveys the results of recent studies of the chemistry of sulfides. The structure and physicochemical properties of sulfides, the methods for their synthesis, as well as their reactions are considered. The bibliography includes 211 references.

I. Introduction

Sulfides constitute one of the simplest classes of organosulfur compounds, which play an extremely important role in organic synthesis. This is due primarily to the presence of the sulfur atom — an active reaction centre with variable valence, the relatively high lability of the C – S bond which may be cleaved by nucleophiles and electrophiles, and also the tendency of sulfur to stabilise the α-carbanionic centre. Together with extensive synthetic possibilities, certain sulfides possess valuable practical properties, which has also aroused an increased interest in the chemistry of sulfides. They have found extensive applications as polymer stabilisers,[1,2] vulcanising agents,[3] pharmaceutical preparations,[4] and biologically active substances.[5] The importance of sulfides in biochemical processes, especially in the metabolism of lipids, is great.[6] In the conversion of the aliphatic acids of lipids into 2-carbon fragments, a key role is assumed by coenzyme A (Co-A), which forms a thioester bond with the aliphatic acid molecule.

Two excellent reviews,[7,8] covering the literature up to 1978, have been devoted to the chemistry of sulfides. However, many new data, which need to be surveyed, have accumulated since the time of their publication. This is in fact the topic of the present review.

II. The structure and physicochemical properties of sulfides

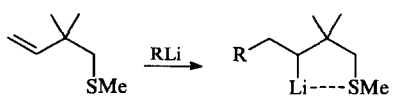
The structure of the groups attached to the sulfur atom exerts a strong influence on the C – S – C bond angle, the C – S bond length, and the dissociation energy of the latter (E_d), which varies over a relatively wide range:[9]

Sulfide	E_d/kcal mol^{-1}
MeS – Me	77.0 ± 1.5
MeS – Et	74.0 ± 1.5
MeS – CH_2Ph	59.4 ± 2.0
PhS – Me	67.4 ± 1.5
AlkS – Bu	71.0 ± 1.5
MeS – Ph	89.2 ± 2.0
MeS – CN	97.0 ± 1.5

The length of the C – S bond in sulfides varies in the range 175 – 180 pm depending on the structure of the group attached to the sulfur atom, while the C – S – C bond angle is 98.9° for dimethyl sulfide and 105.6° for hexafluorodimethyl sulfide.[7] The enthalpy of the C – S bond is 69 kcal mol^{-1}.[9]

Sulfides are $10^{14} - 10^{17}$ times weaker bases than thiolate anions.[7] In contrast to their oxygen analogues, sulfides show a considerable tendency to generate α-carbanions and α-radicals, which has been explained by the increased stabilisation of these species by $p_\pi - d_\pi$ conjugation[7] or by the greater polarisability of sulfur compared with oxygen.[10,11] α-Carbonium ions based on sulfides are less stable than those based on the oxygen analogues. It has been suggested[10,11] that the stabilisation of the carbonium ions is due to the p,π conjugation and, since this stabilisation is directly proportional to the distance separating the two nuclei, the alkoxycarbonium ion is stabilised to a greater extent than the alkylthiocarbonium ion.

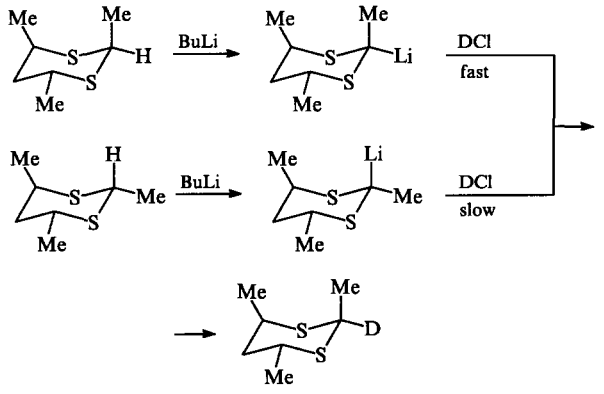
Aliphatic sulfides are very active photoexcitation 'quenching agents'. For example, 1 mol of dibutyl sulfide can prevent the photochemical reduction of 23 mol of benzophenone by alcohols, which has been explained[8] by the formation of the complex $Ph_2CO^{\bullet-}\cdots{}^{+}SBu_2$. According to ^{1}H NMR spectroscopic data obtained using shift reagents,[12] sulfides form unstable complexes with Eu(fod)$_3$. Macrocyclic sulfides are much stronger complex-forming agents for silver ions than macrocyclic ethers but are weaker for alkali metal ions, which is apparently associated with the greater size and lower electronegativity of the sulfur atom compared with oxygen. It has been noted that the addition of organolithium compounds to a nonconjugated carbon – carbon bond becomes possible by virtue of the formation of an alkali metal complex with participation of the sulfur atom.[12]



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1,3-Dithianes assume the twisted boat (twist) conformation more readily than the corresponding O- or C-analogues because nonbonding interactions are weakened in the larger 1,3-dithiane ring, while the torsional barriers are reduced for the C–S bonds compared with those for the C–O and C–C bonds. The twist-form of 3,3,6,6-tetramethyl-1,2,4,5-tetrathiane is actually more stable by 2.1–2.5 kJ mol^{-1} than the chair form. The equilibrium isomerisation of 2-substituted 1,3-dithianes on treatment with butyllithium leads to the formation mainly of isomers with an axial disposition of the substituents. Although such disposition is sterically unfavourable, it occurs even for 2-butyl-1,3-dithiane because lithium tends to occupy the equatorial position.[8] As a consequence of the above feature, there is a possibility of the stereospecific deuteriation of 2,4,6-trimethyl-1,3-dithiane.

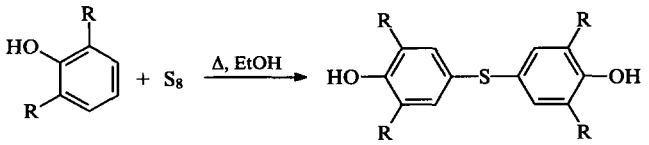


The absorption bands in the UV spectra of alkyl sulfides lie in the region of 200, 220, and 240 nm,[13] while those in the spectra of alkyl aryl sulfides are in the region of 205–230, 235–270, and 275–300 nm.[14] The positions of the absorption bands depend significantly on the structure of the substituents at the sulfur atom and on the nature of the solvent. The long-wavelength absorption is usually very weak and is not characteristic of sulfides. The chemical shift (δ) of the protons in the CH_3S group is in the region of 2 ppm.[15] The mass spectra of alkyl sulfides[16] are characterised by fairly intense peaks due to molecular ions, the intensity of which diminishes with increase in the number of carbon atoms in the molecule and as the sulfur atom moves to one of the ends of the chain. Two types of fragment ions are mainly present: the sulfur-containing ions $[C_nH_{2n+1}S]^+$, $[C_nH_{2n}S]^{\cdot+}$, and $[C_nH_{2n-1}S]^+$ and the hydrocarbon ions $[C_nH_{2n+1}]^+$, $[C_nH_{2n}]^{\cdot+}$, and $[C_nH_{2n-1}]^+$. The main components of the chemical ionisation mass spectra of sulfides[17,18] are the quasi-molecular ions $[M-1]^-$. According to Tokarev et al.,[19] the relative ionisation cross-section of diethyl sulfide is 0.23 (reagent gas—isobutane, 14 Pa, 150 °C).

III. Methods of synthesis of sulfides

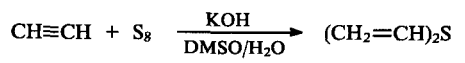
1. Syntheses based on elemental sulfur and its inorganic derivatives

Elemental sulfur is fairly rarely used in the synthesis of sulfides, which is due to the need for its activation or the application of highly reactive aromatic compounds, for example compounds such as dialkylphenols.[16]



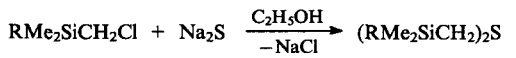
R = Me, Et, Bu^t.

Under chemical activation conditions (a superbasic medium), sulfur reacts with acetylene and its derivatives to form divinyl sulfide.[20]



Unsaturated sulfides are also formed on interaction of unsaturated ethers with organomagnesium compounds and sulfur in the presence of palladium complexes.[21] Under electrochemical activation conditions (decomposing sulfur electrode), elemental sulfur reacts with aromatic ethers, amines, and phenols as well as certain heterocyclic compounds to form the corresponding sulfides.[22,23]

Inorganic sulfur derivatives, for example sodium sulfide, are used much more frequently in the synthesis of sulfides. A whole series of preparative methods for the synthesis of symmetrical sulfides have been developed on the basis of the reaction involving the alkylation and arylation of sodium sulfide by alkyl halides and activated aryl halides. As a rule, these reactions proceed in homophase systems. In the case of heterophase systems, phase transfer catalysts are employed.[24] These methods are applicable also in the synthesis of silicon-containing sulfides.[25]



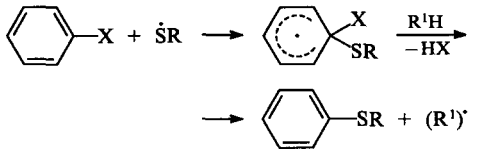
R = Me, Ph.

Another aspect of the use of sodium sulfide in the synthesis of organic sulfides involves its interaction with acetylenic hydrocarbons in the presence of halogen derivatives.[26]



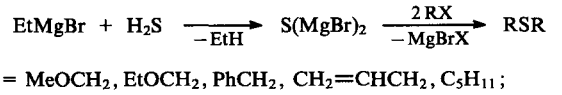
R = H, Ph; $R^1 = HOCH_2CH_2$.

Hydrogen sulfide is much more rarely used in the synthesis of sulfides because its reactions with chloro- and bromo-substituted aromatic and heteroaromatic compounds proceed as a rule at high temperatures to form thiols and other products together with sulfides.[27–30] These reactions proceed via a radical mechanism with the formation of intermediate adduct-radicals stabilised by the π-system of the aromatic ring.[16]



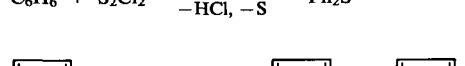
R = H, Ar; X = Cl, Br.

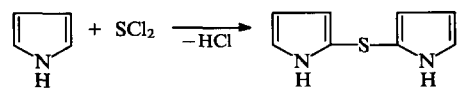
The reaction of hydrogen sulfide with ethylmagnesium bromide, affording bis(bromomagnesium) sulfide, which readily interacts with electrophiles to form organic sulfides, is of preparative interest.[31]



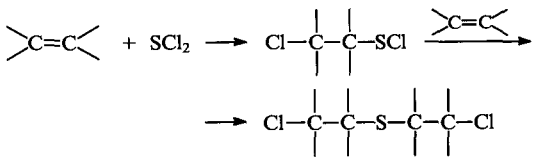
R = $MeOCH_2$, $EtOCH_2$, $PhCH_2$, $CH_2=CHCH_2$, C_5H_{11};
X = Cl, Br.

Among inorganic sulfur derivatives, sulfur monochloride and dichloride are also used in the synthesis of sulfides. The sulfenylation of aromatic and heterocyclic hydrocarbons by these reagents constitutes the basis of a preparative method for the synthesis of symmetrical sulfides.[8]





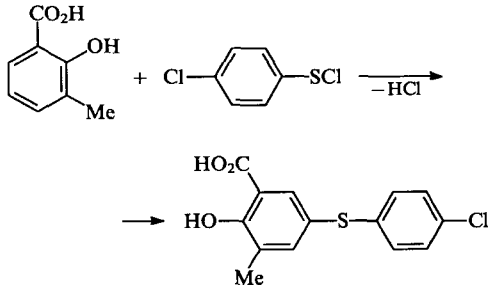
The addition of sulfur dichloride to ethylenic hydrocarbons leads to bis(β-chloroalkyl) sulfides.[16]



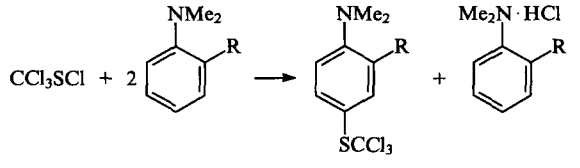
2. Syntheses based on sulfenyl halides

a. Sulfenylation of aromatic and heterocyclic compounds by sulfenyl chlorides

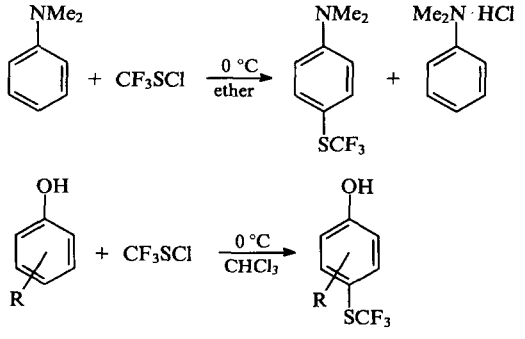
Sulfenyl chlorides react with aromatic hydrocarbons via the S_E2 electrophilic substitution mechanism to form both symmetrical and asymmetric sulfides. Aromatic sulfenyl chlorides react with benzene and its homologues only in the presence of catalysts ($AlCl_3$, $FeCl_3$, Fe, etc.). Sulfenyl chlorides react relatively easily with benzene and naphthalene derivatives containing strong electron-donating substituents (NMe_2, OH, OMe etc.). For example, *p*-chlorobenzenesulfenyl chloride reacts with 6-methylsalicylic acid in the absence of a catalyst to form the corresponding sulfide.[32]



Trichloromethanesulfenyl chloride reacts relatively easily with dimethylaniline and its derivatives, forming the corresponding aryl trichloromethyl sulfides.[33]

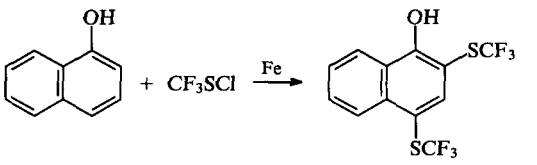


Trifluoromethanesulfenyl chloride reacts with dimethylaniline[4] and with phenol and its homologues[34] even at 0 °C. Under these conditions, the trifluoromethylthio-group adds in the *ortho*- and *para*-positions relative to the substituent.

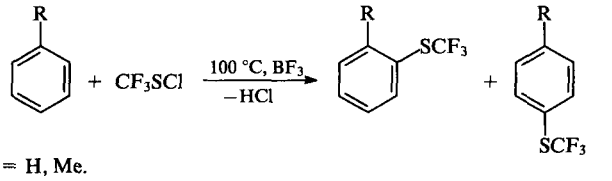


R = H, 2-Me, 3-Me, 2-OH.

The reaction of trifluoromethanesulfenyl chloride with α-naphthol affords 2,4-bis(trifluoromethylthio)naphthol.[35]

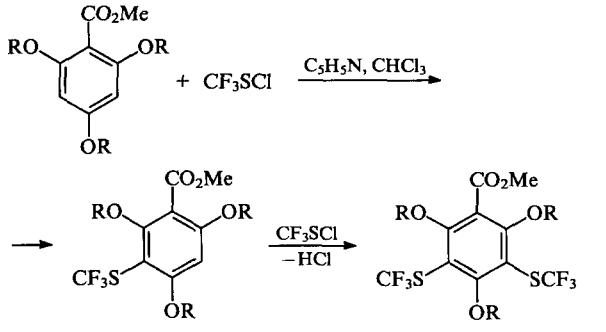


Trifluoromethanesulfenyl chloride reacts with benzene and toluene in the presence of BF_3 at 100 °C in an autoclave, forming phenyl trifluoromethyl sulfide or a mixture of 2- and 4-tolyl trifluoromethyl sulfides.[4,33]

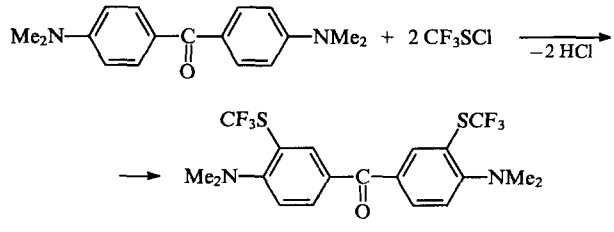


R = H, Me.

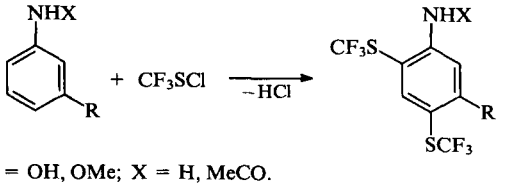
Trifluoromethanesulfonic acid is a more effective catalyst of the trifluoromethanesulfenylation of benzene. Its employment makes it possible to reduce the temperature of the above reaction to 20 °C.[36] The introduction of a second trifluoromethylthio-group into the benzene ring is difficult even in the presence of trifluoromethanesulfonic acid. Trifluoromethanesulfenyl chloride reacts with chlorobenzene under severe conditions in the presence of HF, forming two isomers—*p*- and *o*-chlorophenyl trifluoromethyl sulfides.[36] If there are electron-donating groups (OH, OMe, NMe_2) in the aromatic ring together with electron-accepting groups (MeCO, PhCO, MeOCO, CHO), then one, two, and even three trifluoromethylthio-groups enter into the reaction depending on the conditions.[4,37]



R = H, Me.

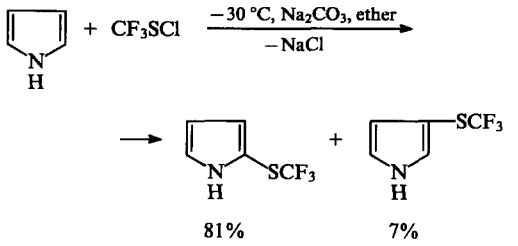


Derivatives of aniline and acetanilide containing the electron-donating OH or OMe groups in the *meta*-position also react readily with trifluoromethanesulfenyl chloride to form bis(trifluoromethylthio)-derivatives.[34]



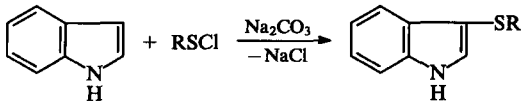
R = OH, OMe; X = H, MeCO.

Similar rules have been established for the interaction of sulfenyl chlorides with cyclic compounds.[4] The presence in the latter of a high π-electron density promotes this reaction. For example, pyrrole reacts with trifluoromethanesulfenyl chloride even at −30 °C, forming 2-trifluoromethylthiopyrrole and a small amount of 3-trifluoromethylthiopyrrole.[37–39]



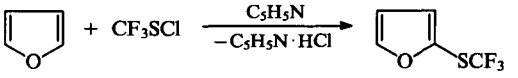
81% 7%

In the presence of catalytic amounts of a perfluoroalkanesulfonic acid, two, three, and even four trifluoromethylthio-groups may be introduced into the pyrrole ring.[38] In indole, the substitution of a hydrogen atom by the sulfenyl group takes place in the 3-position.[37, 40]

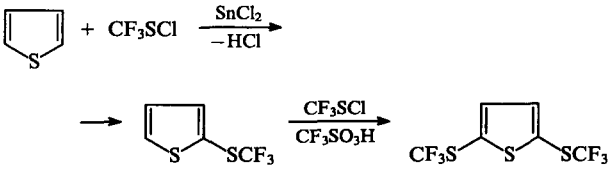


R = CF_3, 2(3,4)-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$.

2-Trifluoromethylthiofuran is the product of the reaction of furan with trifluoromethanesulfenyl chloride in the presence of pyridine.[39]



Trifluoromethanesulfenyl chloride reacts with thiophene, giving rise to 2-(trifluoromethylthio)thiophene or 2,5-bis(trifluoromethylthio)thiophene depending upon which catalyst is employed.[36, 39, 41]



b. Sulfenylation of C-nucleophiles

Sulfenyl chlorides react vigorously with organomagnesium compounds via the nucleophilic substitution mechanism, forming sulfides.[33]

$$RSCl + R^1MgX \longrightarrow RSR^1 + MgXCl$$

R = CCl_3, CF_3; R^1 = Et, Ph, 3(4)-MeC_6H_4;
X = Cl, Br.

Under these conditions, a small amount (up to 15%) of halohydrocarbons is formed as a rule, which hinders the isolation of the sulfides obtained. Organomercury compounds react with sulfenyl chlorides similarly to organomagnesium compounds.[42] The substitution of the chlorine atom at the sulfur atom by a hydrocarbon group is then accompanied by the simultaneous replacement of the HgCl fragment by chlorine and also by demercuration.

$$RSCl + p\text{-}R^1C_6H_4HgCl \longrightarrow RSC_6H_4R^1\text{-}p + p\text{-}R^1C_6H_4Cl + PhR^1$$

R = CF_3; R^1 = H, Me, MeO, Cl, NO_2.

Electron-accepting groups promote the formation of sulfides, whereas electron-donating groups promote the formation of halo-derivatives. A method of synthesis of sulfides involving the interaction of arenesulfenyl chlorides with perfluoro-*tert*-butylcaesium in acetonitrile or diglyme,[43, 44] and also its interaction with perfluoromethyl(trimethyl)silane in tetrahydrofuran,[45] has been described in the literature. The yield of the sulfides is 75%–85%.

$$RC_6H_4SCl + (CF_3)_3CCs \xrightarrow[-CsCl]{} RC_6H_4SC(CF_3)_3$$

R = H, 3(4)-F, 4-Cl, 2(3,4)-NO_2, 3(4)-COOMe.

$$RC_6H_4SCl + Me_3SiCF_3 \longrightarrow RC_6H_4SCF_3 + Me_3SiCl$$

R = 4-Cl, 4-NO_2.

Treatment of copper acetylide with arenesulfenyl chlorides leads to the formation of alkynyl aryl sulfides.[8]

$$RC{\equiv}CCu + ArSCl \longrightarrow RC{\equiv}CSAr$$

R = H, Me; Ar = Ph, *p*-MeC_6H_4.

A whole series of methods of synthesis of sulfides are based on the sulfenylation of CH acids by sulfenyl chlorides and other sulfenylating agents. The choice of the reaction conditions is dictated both by the nature of the CH acid and that of the sulfenyl chloride. For example, the sulfenylation of nitromethane by trichloromethanesulfenyl chloride is carried out at 0 °C in an aqueous alkaline medium.[33]

$$CCl_3SCl + CH_3NO_2 \xrightarrow[-NaCl]{0\ ^\circ C,\ NaOH} CCl_3SCH_2NO_2$$

Nitromethane reacts with benzenesulfenyl chloride[46] in absolute alcohol in the presence of sodium ethoxide, while its reaction with *o*-nitrobenzenesulfenyl chloride takes place in anhydrous benzene in the presence of triethylamine and affords the corresponding sulfides. Diacetyl- and dibenzoyl-methanes and acetoacetic and malonic acid esters interact with arenesulfenyl chloride in anhydrous benzene in the absence of bases,[47–49] whereas diphenylmethane[50] and dicyanomethane[51] require the use of triethylamine.

$$ArSCl + CH_2XY \xrightarrow[-HCl]{} ArSCH(X)Y$$

Ar = Ph, 4-MeC_6H_4, 2(4)-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$;
X = Y = Ph, MeCO, PhCO, EtOCO, CN;
X = MeCO, Y = EtOCO;
X = H, Y = NO_2;
X = NO_2, Y = 2-$NO_2C_6H_4$.

The sulfenylation of tris(trifluoromethyl)methane by benzenesulfenyl chloride also takes place in the presence of triethylamine.[52]

$$PhSCl + HC(CF_3)_3 \xrightarrow[-Et_3N\cdot HCl]{Et_3N} PhSC(CF_3)_3$$

The trifluoromethanesulfenylation of the CH acids RCX.CH_2R^1 (X = O, NH; R = Ph, Me; R^1 = $CONH_2$, CN, C(S)NH.C_6H_4Br-*p*) is carried out in anhydrous chloroform at 0–20 °C with the use of bases.[53]

Numerous studies have been devoted to the sulfenylation of phosphorus-containing CH acids and their anions, studies that are associated with the search for new biologically active preparations.[54] For example, a study has been made[55] of the interaction of perhalomethanesulfenyl chlorides with the anions of tetraalkyl methylphosphonates, generated by treating tetraalkyl methylphosphonates with butyllithium, sodium hydride, or metallic sodium. The formation of sulfenylation and chlorination products was established. In the case of dichlorofluoro- and chlorodifluoromethanesulfenyl chlorides, sulfenylation products were obtained under these conditions, in which the trihalomethanesulfenyl groups are enriched in fluorine compared with those in the initial sulfenyl chlorides.

$$[(RO)_2P(O)]_2CHM + CCl_{3-n}F_nSCl \xrightarrow{AlCl_3}$$
$$\longrightarrow [(RO)_2P(O)]_2CHSCCl_{3-n}F_n + [(RO)_2P(O)]_2CHCl +$$
$$+ [(RO)_2P(O)]_2CHSCCl_{2-n}F_{n+1} + [(RO)_2P(O)]_2CHSCF_3$$

R = Pr^i; M = Li, Na.

It is believed[55] that the products with a fluorine-enriched trihalomethanesulfenyl group are formed as a result of the substitution of chlorine atoms by fluorine in the initial sulfenyl chloride and not in the sulfenylation products. The fluoride anion, appearing on decomposition of the trihalomethylthio-anion, which is a side product in the chlorination of tetraalkyl methylenediphosphonate, acts as the fluorinating agent under these conditions.

$$[(RO)_2P(O)]_2CHM + CCl_{3-n}F_nSCl \longrightarrow$$
$$\longrightarrow [(RO)_2P(O)]_2CHCl + CCl_{3-n}F_nS^-$$
$$CCl_{3-n}F_nS^- \longrightarrow Cl_{3-n}F_{n-1}C{=}S + F^- + M^+$$
$$CCl_{3-n}F_nSCl + F^- \longrightarrow CCl_{2-n}F_{n+1}SCl + Cl^-$$

The fraction of the chlorination products increases in the following sequence: $CF_3SCl < CF_2ClSCl < CFCl_2SCl$. This has been explained[54,55] by the increase in the same sequence in the steric hindrance to nucleophilic attack on the sulfur atom by the carbanion. It has been noted[56] that, when benzenesulfenyl chloride is added to an excess of sodium diethyl cyanomethylphosphonate, the corresponding sulfide is formed almost exclusively.

$$(EtO)_2P(O)\underset{CN}{\underset{|}{C}}HNa + ClSPh \xrightarrow[-NaCl]{} (EtO)_2P(O)\underset{CN}{\underset{|}{C}}H{-}SPh$$

The similar interaction of α-substituted ethylphosphonic acid esters with benzenesulfenyl chloride leads to the corresponding sulfides in an almost quantitative yield.[57]

$$(EtO)_2P(O)\underset{R}{\underset{|}{C}}HMe + ClSPh \xrightarrow[-NaCl]{NaH} (EtO)_2P(O)\underset{R}{\overset{Me}{\overset{|}{\underset{|}{C}}}}{-}SPh$$

R = CN, COOEt.

The reaction of triisopropyl phosphonoacetate with benzenesulfenyl chloride in the presence of aluminium isopropoxide[58] leads to the substitution of one or two hydrogen atoms by the phenylthio-group depending on the reactant ratio.

$$(Pr^iO)_2P(O)CH_2COOPr^i \xrightarrow{Al(OPr^i)_3}$$
$$\xrightarrow[2\ PhSCl]{PhSCl} \begin{matrix}(Pr^iO)_2P(O)CH(SPh)COOPr^i \\ (Pr^iO)_2P(O)C(SPh)_2COOPr^i\end{matrix}$$

The reaction of the chloride of diethoxyphosphorylacetic acid with benzenesulfenyl chloride takes place without a solvent. After treatment with water or methanol, the product is converted into α-diethoxyphosphoryl-α-phenylthioacetic acid or its ethyl ester (in 50% yield).[59]

$$(EtO)_2P(O)CH_2COCl + PhSCl \xrightarrow[MeOH]{H_2O} \begin{matrix}(EtO)_2P(O)\underset{COOH}{\underset{|}{C}}HSPh \\ (EtO)_2P(O)\underset{COOMe}{\underset{|}{C}}HSPh\end{matrix}$$

Phosphorus ylides readily exchange the hydrogen atom of the methylene group for an alkylthio- or arylthio-group.[60]

$$Ph_3P{=}CHR + R^1SCl \xrightarrow[-HCl]{} Ph_3P{=}\underset{R}{\underset{|}{C}}{-}SR^1$$

R = Me, EtOCO, CN, PhCO; R^1 = Alk, Ar.

Depending on the reactant ratio, it is possible to substitute one or two hydrogen atoms by the phenylthio-group in methylenetriphenylphosphorane.[60]

$$Ph_3P{=}CH_2 \xrightarrow[2\ PhSCl]{PhSCl} \begin{matrix}Ph_3P{=}CHSPh + HCl \\ Ph_3P{=}C(SPh)_2 + 2\,HCl\end{matrix}$$

Together with sulfenyl chlorides, other sulfenylating agents are also used in the reactions with C-nucleophiles. For example, aryl thiocyanates have been employed successfully for the sulfenylation of perfluorocarbanions[61] and organomagnesium compounds.[61,62] The yields of sulfides are then 50%–55%.

$$XC_6H_4SCN \xrightarrow[-KCN]{(CF_3)_2CFK} XC_6H_4SCF(CF_3)_2$$
$$XC_6H_4SCN \xrightarrow[-Mg(CN)I]{BuMgI} XC_6H_4SBu$$

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

Two versions of the synthesis of alkyl trichloromethyl sulfides from alkyl thiocyanates have been developed. The first involves the interaction of alkyl thiocyanates with chloroform under the conditions of phase transfer catalysis.[63]

$$RSCN + CHCl_3 \xrightarrow[-HCN]{} RSCCl_3$$

R = Me, Et.

The second version involves the interaction of alkyl thiocyanates with perchlorocarbanions obtained from perhalomethanes by treatment with KOH in the presence of phase transfer catalysts such as, for example, tetrabutylammonium bromide.[64]

$$CCl_3X + OH^- \underset{}{\overset{Bu_4NBr}{\rightleftharpoons}} \bar{C}Cl_3 \xrightarrow{MeSCN} MeSCCl_3$$

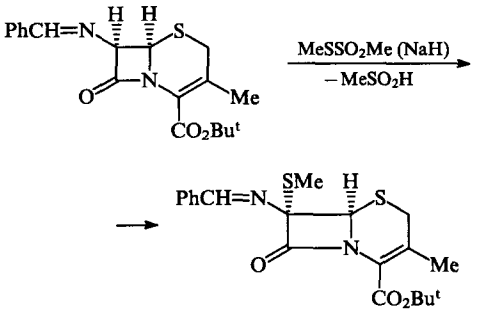
X = Cl, Br.

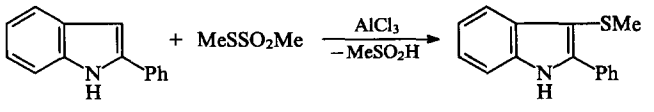
It has been noted[65] that in the presence of bases certain CH acids are sulfenylated by the RSH–CCl_4 system.

$$RSH + Na\underset{Y}{\underset{|}{\overset{X}{\overset{|}{C}}}}R^1 \xrightarrow[-CHCl_3]{CCl_4} RS\underset{Y}{\underset{|}{\overset{X}{\overset{|}{C}}}}R^1 + NaCl$$

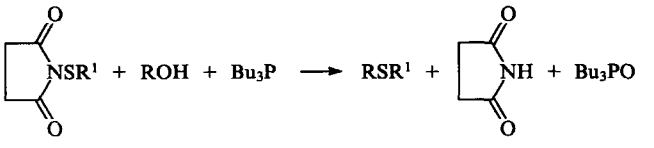
R = Alk, Ar; R^1 = H, Alk, Ar; X = Y = COMe, COOEt.

The use of thiolo-esters of sulfonic acids [66] and sulfenamides [67] as sulfenylating agents for CH acids has not come to be widely employed in the synthesis of sulfides owing to the formation of side products which hinder the isolation of the sulfides. However, in rare instances these compounds are nevertheless used as mild sulfenylating agents. For example, the methyl thiolo-ester of methanethiosulfonic acid is used to introduce the methylthio-group into certain derivatives of cephalosporin and indole. [8]



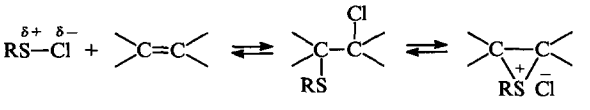


Certain sulfenamides form sulfides on interaction with alcohols in the presence of trialkylphosphines. [8]

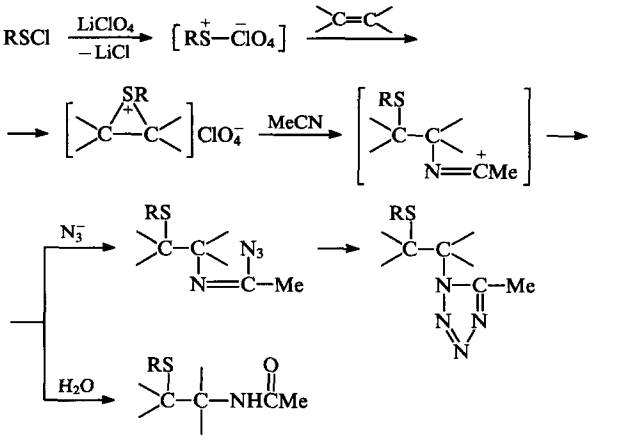


c. Addition of sulfenyl chlorides to the C = C bond

Sulfenyl chloride adds smoothly to alkenes with formation of β-chlorosulfides, [7,68,69] which are the starting materials for the synthesis of saturated and unsaturated sulfides. [69] It has been suggested that this reaction proceeds via an Ad_E2 mechanism, in which the cationic intermediate is an episulfonium ion, and leads as a rule to stereospecific *trans*-addition.

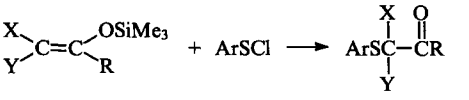


Sulfenyl chlorides are relatively weak electrophiles and the intermediate episulfonium cation has a small positive charge, which does not allow it to react with weak nucleophiles. A method developed by Zefirov and coworkers, [70,71] involving the coupled addition of sulfenyl chlorides to a double bond in the presence of a strong electrophile, for example lithium perchlorate, which increases the effective electrophilicity of sulfenyl chlorides ('doping process'), is therefore of interest. The episulfonium cation formed in this process reacts even with a weak nucleophile such as acetonitrile, affording an immonium ion, which is converted into the final products on treatment with various reagents.

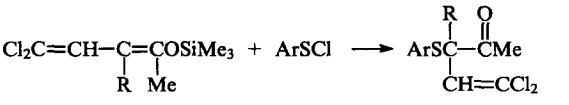


This reaction has been investigated for cyclohexene, norbornene, hept-1-ene and other olefins.

A novel method has been developed for the synthesis of aryl β-oxoalkyl sulfides involving the interaction of vinyloxysilanes [72–74] and divinyloxysilanes [75] with arenesulfenyl chlorides. The reaction proceeds via stages involving the 1,2-addition of ArSCl and the elimination of chlorotrimethylsilane. [74]

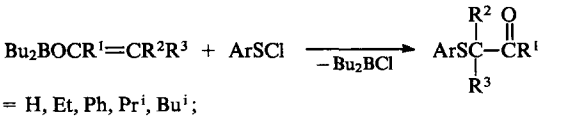


X = H, Cl, Br; Y = Cl; R = H, Bu^t, Ph, 4-ClC$_6$H$_4$, 4-BrC$_6$H$_4$;
Ar = 4-MeC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-NO$_2$C$_6$H$_4$.



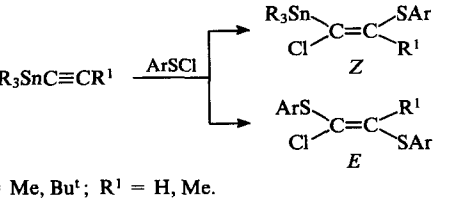
R = H, Ac, COOEt;
Ar = 4-MeC$_6$H$_4$, 4-ClC$_6$H$_4$.

Arenesulfenyl chlorides react similarly with the enols of dibutyl borinates. [76]



R^1 = H, Et, Ph, Pr^i, Bu^i;
R^2 = H, Me, Et, Pr; R^3 = H, Me, Ph;
R^3 = H, Me, Ph; Ar = Ph.

Arenesulfenyl chlorides react with trialkylstannylacetylenes to form either the products of addition to the triple bond or the products of their subsequent arylthiodestannylation—(*E*)-1,2-bis(arylthio)chloroethylenes. [77] The addition reaction takes place stereospecifically and regioselectively regardless of the structure of the alkyl groups at the tin atom.



R = Me, Bu^t; R^1 = H, Me.

3. Syntheses of sulfides from thiols

The syntheses of sulfides from thiols have been described in detail in a previously published review by the author [78] and in the literature quoted therein and they will not therefore be considered here.

4. Syntheses from disulfides

a. Cleavage of disulfides

The cleavage of disulfides by nucleophiles has not so far been used widely in the syntheses of sulfides owing to the formation of a series of side products. Nevertheless, some of these methods can be recommended for preparative purposes. For example, disulfides are frequently cleaved in the presence of NaCN in order to synthesise cyanoaryl sulfides.[7]

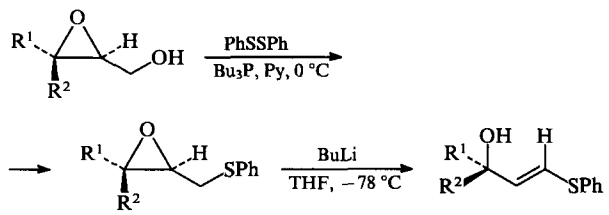
$$ArSSAr + NaCN \xrightarrow{\Delta} ArSCN + ArSNa$$

In the presence of alcohols, such cleavage is accompanied by the formation of sulfides containing alkoxy- and imino-groups.[8]

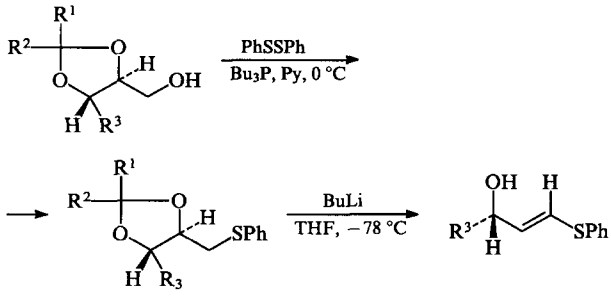
$$ArSSAr + ROH + \bar{C}N \longrightarrow ArSC(=NH)OR$$

Ar = Ph, *p*-MeC_6H_4; R = Me, Et.

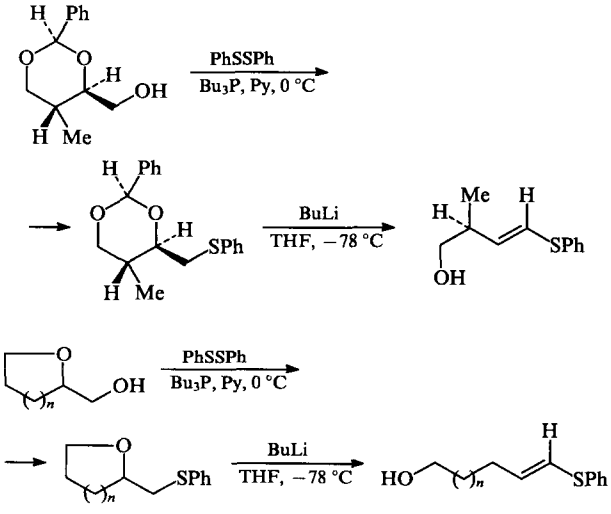
The cleavage of diphenyl disulfide by tributylphosphine and the addition of the PhS radical to oxacyclic alcohols are used in the synthesis of ω-hydroxyalk-1-enyl phenyl sulfides.[79]



$R^1 = CH_2{=}CH(CH_2)_3$; R^2 = H;
R^1 = Ph, R^2 = H.



$R^1 = R^2$ = Me, R^3 = $BuOCH_2$;
$R^1 = R^2$ = Ph, R^3 = $BuOCH_2$;
$R^1 = R^2$ = Me, R^3 = $Me(CH_2)_4$.



n = 1, 2.

An oxidative decarboxylation method has been developed in recent years on the basis of the cleavage of dialkyl disulfides in the presence of sodium hydride in dimethyl sulfoxide (DMSO) or tetrahydrofuran (THF). It involves the replacement of a carboxy- or ester-group by an alkylthio-group.[80,81]

$$XCH_2COOR \xrightarrow[NaH,\ DMSO\ (THF)]{MeSSMe} XCH_2SMe$$

X = $(EtO)_2PO$, $PhSO_2$;
R = H, Et.

b. Interaction of disulfides with organometallic compounds

The interaction of disulfides with organomagnesium compounds leads to the formation of mixtures of sulfides and thiols, which is sometimes used in the synthesis of sulfides.[7]

$$RSSR + R^1MgX \longrightarrow RSMgX + R^1SR$$

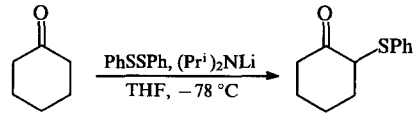
R = R^1 = Et, Ph.

Disulfides react similarly with organolithium compounds.[7,82]

$$RSSR + R^1Li \longrightarrow RSR^1 + RSLi$$

R = Me, Et, C_6H_{11}, $PhCH_2$;
R^1 = HC ≡C, $(EtO)_2CHC{\equiv}C$, $ClC{\equiv}C$, 2-$(Me_2NCHMe)C_6H_4$.

The reaction of disulfides with organolithium compounds constitutes the basis of one of the methods for the introduction of the sulfide group, which is used widely in multistep organic syntheses. For example, in order to introduce the phenylthio-group in the α-position in cyclic ketones, the latter are treated with lithium diisopropylamide in the presence of diphenyl disulfide in THF.[16]



c. Alkylation and arylation of disulfides

The alkylation of diphenyl disulfides with triethyloxonium tetrafluoroborate leads to a sulfonium salt, the hydrolysis of which affords a mixture of two sulfides—PhSEt (51%) and *p*-$PhSC_6H_4SEt$ (30%).[8] Disulfides are also alkylated by alkyl fluorides in the presence of SbF_5 and trifluoroiodomethane in liquid ammonia on exposure to UV light.[83]

$$XC_6H_4SSC_6H_4X + CF_3I \xrightarrow{NH_3,\ h\nu} XC_6H_4SCF_3$$

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

The yields of sulfides are 12% – 36% for X = H or 4-Cl and 58% and 72% respectively for X = 2-NO_2 and 4-NO_2.

Disulfides are arylated by aryl iodides in diphenyl ether at 230–270 °C.[84]

$$PhSSPh + ArI \xrightarrow{Ph_2O,\ 230-270\ ^\circ C} PhSAr$$

Ar = Ph, *p*-MeC_6H_4.

c. Desulfurisation of disulfides

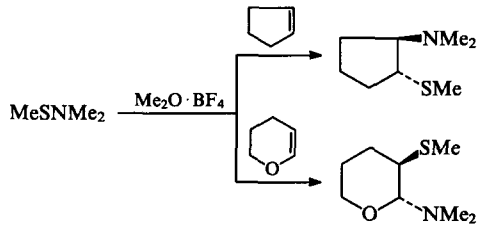
The desulfurisation of certain disulfides usually proceeds on heating,[85] whereas the conversion of other disulfides into sulfides requires the use of desulfurisation reagents, for example $(Et_2N)_3P$ or $Et_4N^+F^-$.[86] In the presence of phosphines, thiolocarbonates and xanthates are also converted into sulfides.[8]

$$ArSSAr \xrightarrow[-S]{\Delta} ArSAr$$

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

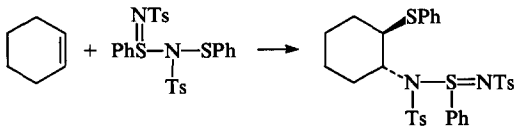
5. The syntheses from sulfenamides

The heterolytic cleavage of the S–N bond in sulfenamides in the presence of olefins is accompanied by the addition of the resulting fragments to the double bonds of the olefins with formation of aminosulfides.[87] Thus the heterolytic cleavage of the S–N bond in *N*-(dimethyl)methylsulfenamide in nitromethane in the presence of cyclopentene or 3,4-dihydro-2*H*-pyran leads to the formation of *trans*-1-dimethylamino-2-methylthiocyclopentane or *trans*-2-dimethylamino-3-methylthiotetrahydropyran.[88,89]



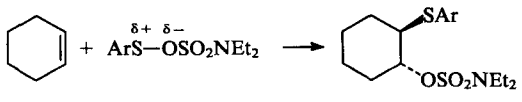
The addition of the sulfenamides $PhSNR^1R^2$ [R^1 = H, R^2 = Bu^t, $R^1+R^2 = (CH_2)_4$, $(CH_2)_2O(CH_2)_2$] to the C=C bond of cyclohexene, octene, and indene[90,91] also takes place preferentially in the *trans*-position. Strong proton-donating acids or Lewis acids are catalysts of the aminosulfenylation of olefins.

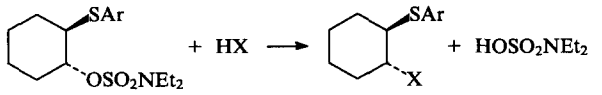
Under the conditions of acid catalysis, *N*-arenesulfenylamidines of sulfinic acids add to the C=C bonds of cyclohexene with formation of aminosulfides.[92]



The reactivity of sulfenamides in relation to olefins in the heterolytic addition reaction increases with increased electrophilicity of the sulfur atom, which can be achieved by inserting sulfur dioxide in the S–N bond of sulfenamides.[93] Using this procedure, Zefirov et al.[94] achieved for the first time the sulfamatosulfenylation of olefins, which involves the interaction of sulfenamides with sulfur dioxide in an inert solvent at a reduced temperature (–85 °C) with subsequent addition of the insertion products to the C=C bond of olefins. The reaction involving the sulfamatosulfenylation of cyclohexene is stereospecific and leads to the *trans*-1,2-adduct, which is converted into the corresponding sulfides on treatment with inorganic and organic acids.[94]

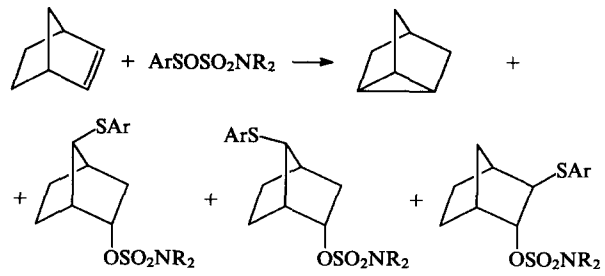
$$ArSNEt_2 + SO_3 \xrightarrow{-85\ ^\circ C,\ CH_2Cl_2} ArSOSO_2NEt_2$$

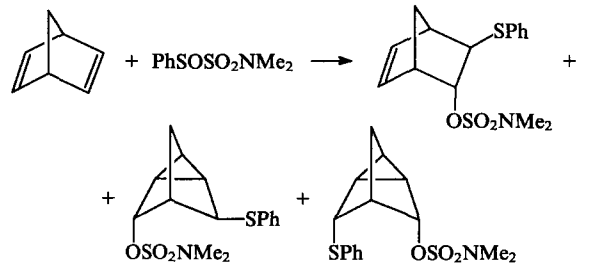




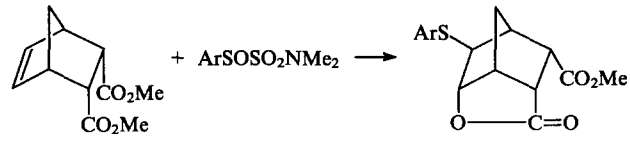
X = Br, MeCOO, CF_3COO, HCOO.

The sulfamatosulfenylation of norbornene and norbornadiene[95] is accompanied by a rearrangement of the carbon skeleton, which ultimately leads to a mixture of several products.

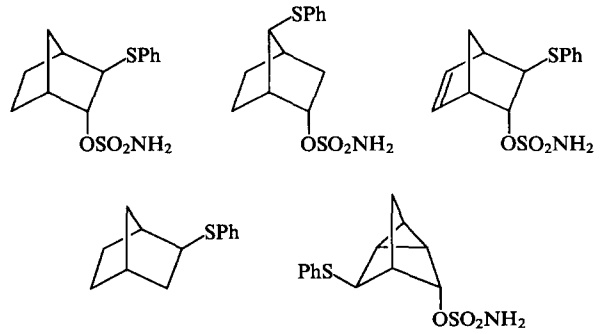




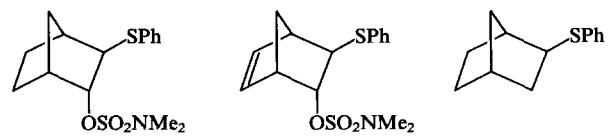
In the sulfamatosulfenylation of dimethyl *endo-cis*-bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylate, the adducts cyclise with formation of arylthiolactones.[95]



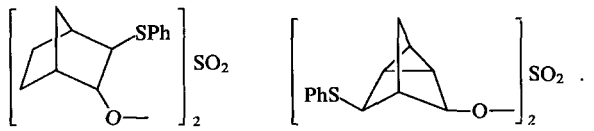
The addition of *N,N*-dimethylbenzenesulfinamide to the olefins RCH = CH_2 (R = H, C_5H_{11}, Ph) in chloroform in the presence of the sulfur trioxide–pyridine complex at 20–25 °C leads to a mixture of two aminosulfides: $RCH(SPh)CH_2NMe_2$ and $RCH(NMe_2)CH_2SPh$.[96,97] It has been suggested[97] that these compounds are formed as a result of the rearrangement of the esters of *N,N*-dimethylsulfamic acid formed in the first stage of the addition reaction. The reaction of the sulfenamide $PhSNEt_2$ with cyclohexene and sulfamic acid in acetonitrile at 90–100 °C affords an adduct, the treatment of which with 10% HCl leads to the hydrochloride of *trans*-2-phenylthiocyclohexylamine.[98] In the case of norbornene and norbornadiene,[99] a mixture of the following products is formed:



Together with the expected products



the interaction of norbornene and norbornadiene with *N,N*-dimethylbenzenesulfenamide in the presence of $K_2S_2O_7$ affords also[100]

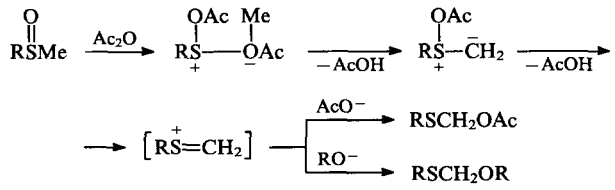


Consequently in the reaction of sulfenamides with SO_3 liberated from the pyrosulfate anion, the generation of the sulfenyl species PhS^+ is accompanied by the simultaneous formation of two counterions — the sulfate and sulfamate anions.

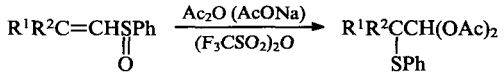
Ethyl benzenesulfenate also reacts with SO_3 in chloroform at −60 °C to form the highly reactive electrophile $PhSOSO_2OEt$, the reaction of which with norbornene and camphene affords a mixture of stereoisomeric sulfides.[101]

6. Syntheses from sulfoxides

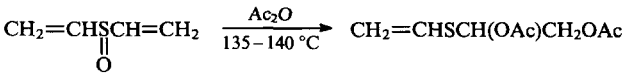
Sulfoxides are usually obtained from sulfides and the reduction of these compounds is therefore not used as a rule to synthesise simple sulfides. Other reactions of sulfoxides, which lead to the formation of sulfides whose structure differs from those of the sulfides used to synthesise the initial sulfoxide, are of preparative importance. For example, the Pummerer rearrangement of sulfoxides on treatment with acetic anhydride in the presence of alcohol leads to α-alkoxyalkyl sulfides, whereas in the absence of alcohol the formation of α-acetoxyalkyl sulfides is observed.[80]



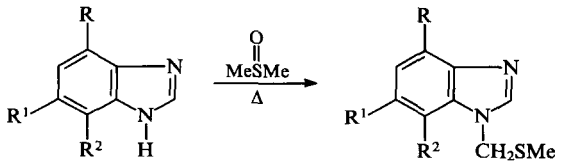
The rearrangement of vinyl sulfoxide[102] and divinyl sulfoxide[103] in acetic anhydride leads to diacetoxyalkyl sulfides.



R^1 = Me, Et, 4-MeC_6H_4, 4-ClC_6H_4, 3(4)-$MeOC_6H_4$;
R^2 = H, Me.



A convenient preparative method of synthesis of methyl sulfides has been developed. It involves the interaction of dimethyl sulfoxide with benzimidazole derivatives.[104]



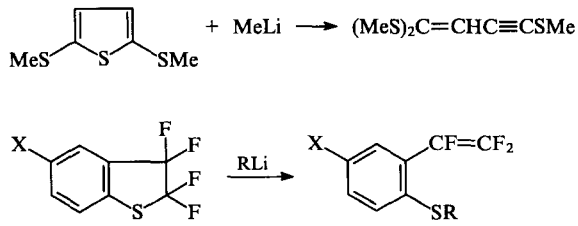
R = H, Me; R^1 = H, NO_2; R^2 = H, NO_2.

Dimethyl sulfoxide reacts similarly with phthalimide, isatin, saccharin, and pyridopyrimidines.[105]

7. Other methods of synthesis of sulfides

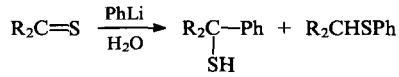
A preparative method of synthesis of bis(*o*-arylthiophenyl) sulfides by the reaction of 5-(4-R-phenyl)thianthrenium perchlorates (R = OMe) with thiophenols RC_6H_4SH (R = 4-Me, 4-MeO, 2-Cl, 2-NH_2) in THF in the presence of sodium hydride has been described.[106]

Polyfunctional sulfides are sometimes synthesised by opening the rings of sulfur-containing heterocyclic compounds on treatment with organolithium compounds.[8,107]



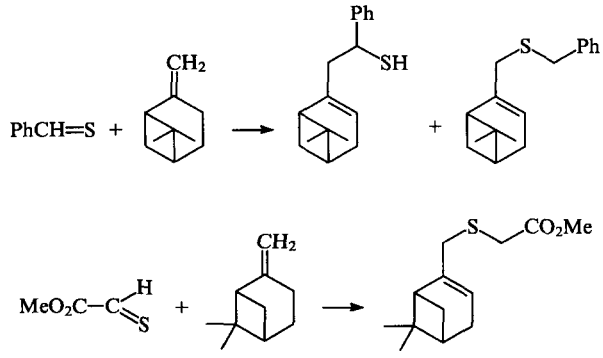
R = Alk, Ar; X = H, Br, Alk.

In the reactions of thiones with organometallic compounds,[78] there is a possibility of addition both to the carbon atom and to the sulfur atom, which results in the formation of a mixture of tertiary thiols and isomeric sulfides.

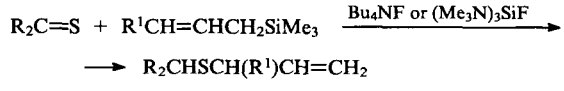


R = Bu^t.

The addition of thiones to the double bond of pinenes also leads to the corresponding sulfides.[9]

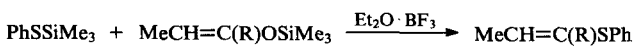


The interaction of thiones with silylated olefins, induced by the fluoride ion, is accompanied by the elimination of the silyl fragment and the formation of allyl sulfides.[108,109]



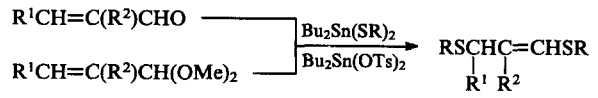
R = 2-MeC_6H_4; R^1 = H, Ph, PhMeCH.

In the presence of the complex $Et_2O.BF_3$, phenylthiosilanes react with alkenyl silyl ethers to form vinyl sulfides.[110,111]



R = Alk, *cyclo*-Alk.

It has been noted[112] that the interaction of alkyl(aryl)-thiostannanes with α,β-unsaturated aldehydes or unsaturated acetals leads to the formation of 1,3-di-alkyl(aryl)thiopropenes in the form of a mixture of (*Z*)- and (*E*)-isomers.



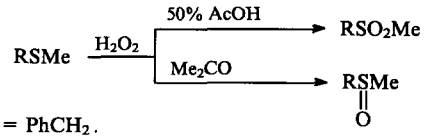
R = Me, Ph, C_6H_{11}; R^1 = H, Me, Pr; R^2 = H, Me, Et.

IV. Reactions of sulfides

1. Reactions involving an increase in the valence of sulfur

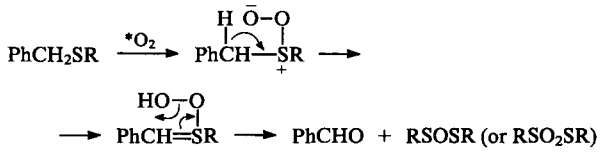
a. Oxidation of sulfides to sulfoxides

Mainly reagents of two types are used to convert sulfides into sulfoxides:[7,113] derivatives of peroxyacids [*m*-chloroperbenzoic and peroxydodecanoic acids activated by manganese(IV) peroxide and sodium periodate] and compounds which serve as sources of a halogen (*tert*-butyl hypochlorite, *N*-bromo- and *N*-chloro-succinimides, 1-chlorobenzotriazole, chlorine, etc.). Individual examples of the use of other reagents are also known, for example nitric acid,[4] cerium ammonium nitrate,[7] hydrogen peroxide in the presence of tellurium dioxide,[114] urea and phthalic anhydride,[115] *o*-iodosylbenzoic acid,[116] tetranitromethane,[117] the ozonides of phosphites,[118] and peroxides.[119] The use of hydrogen peroxide as the oxidant can lead to sulfoxides or sulfones depending on the conditions.[7]

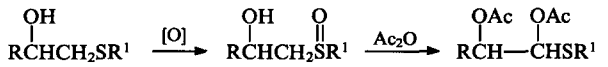


R = $PhCH_2$.

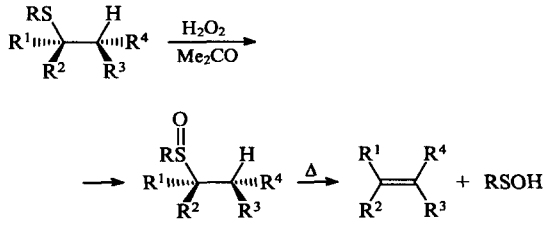
The photochemical oxidation of alkyl benzyl sulfides leads to the formation of a mixture of products, one of which is benzaldehyde.[120]



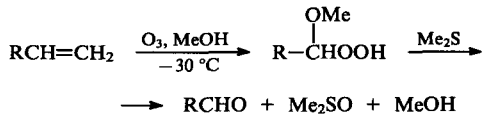
The oxidation of β-hydroxyalkyl sulfides leads to the formation of sulfoxides capable of undergoing the Pummerer rearrangement on heating in acetic anhydride.[8]



Taking into account the tendency of sulfoxides to undergo thermal *cis*-elimination, the oxidation of sulfides to sulfoxides is used in organic synthesis to convert sulfides into alkenes.[16]

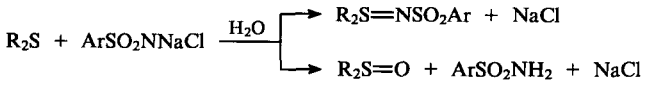


Dimethyl sulfide is used to reduce hydroperoxides.[8]



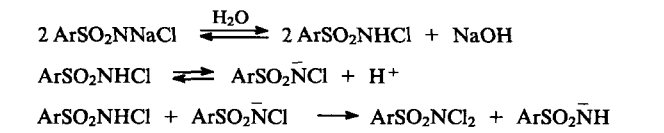
b. Oxidative imination of sulfides

The reactions accompanied by the oxidation of an element and the formation of the imino-group have come to be called oxidative imination.[121] The oxidative imination of sulfides by sodiochloroamides of sulfonic acids proceeds as a rule in aqueous media. Together with sulfilimines, sulfoxides are also formed in this reaction.

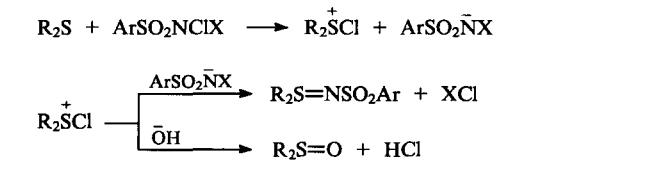


R = Alk, Ar, Het.

The ratio of sulfilimines and sulfoxides depends on the nature of the groups at the sulfur atom in the initial sulfide, the pH of the medium, and the nature of the solvent employed. It has been suggested[122] that the sulfonic acid sodiochloroamide is converted in an aqueous alcoholic medium via a reversible reaction into *N*-chlorosulfonamide (rapidly) and *N,N*-dichlorosulfonamide (slowly), which are fairly reactive electrophiles.

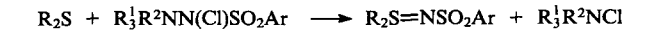


The reaction of a sulfide with *N*-chlorosulfonamide or *N,N*-dichlorosulfonamide[123–126] affords the chlorosulfonium cation R_2S^+Cl, which interacts with the sulfonamide anion $ArSO_2N^-X$ (X = H, Cl) to form a sulfilimine, whereas the hydrolysis of the chlorosulfonium cation leads to sulfoxides.[127]



R = H, Cl.

A low acidity of the medium promotes the conversion of the sulfonic acid sodiochloroamide into the more reactive *N*-chloro- and *N,N*-dichlorosulfonamides, but it reduces the probability of the existence of the sulfonamide anion. According to Tsujihara et al.,[128] pH 6 is optimum in the imination of dialkyl and alkyl aryl sulfides by the sodiochloroamide of toluene-*p*-sulfonic acid. Since aqueous solutions of sulfonic acid sodiochloroamides are alkaline, the addition of a small amount of acetic acid to the reaction medium increases the yield of sulfilimines.[128] In view of the sparing solubility of sulfides in water, aqueous solutions of methanol, acetone, and dioxan as well as two-phase systems, for example water–methylene chloride, are used for their imination, which naturally reduces the yield of sulfilimines and promotes the formation of sulfoxides. The use of anhydrous organic solvents, for example methylene chloride, as the reaction medium and of *N*-chloro-*N*-(tetraalkylamino)arenesulfonamides, readily soluble in these solvents, instead of sulfonic acid sodiochloroamides, leads to the formation of sulfilimines in a quantitative yield.[129]



R = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, $PhCH_2$;
R^1 = Me, Bu; R^2 = Bu, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{18}H_{37}$.

An increase in the yield of sulfilimines in the case where two-phase reaction media are employed is also promoted by phase transfer catalysts.[130]

The susceptibility of the sulfur atom in the sulfide to electrophilic attack by the chlorine cation is directly related to the electron density on the sulfur atom, which depends on the nature

of the substituents. Electron-accepting groups at the sulfur atom hinder the imination reaction or preclude it altogether. Because of this, the search for and development of procedures designed to increase the electron density on the sulfur atom in sulfides is important from both theoretical and synthetic points of view. Analysis of the effective charges in the molecule of methanethiol and its carbanion, obtained as a result of quantum-mechanical calculations by the CNDO/2 method, showed[121,131] that one of these procedures involves the creation of an α-C-anionic centre in the sulfide molecule. The possibility, in principle, of arenesulfonylimination of aryl diacylmethyl sulfides containing a mobile α-H atom together with electron-accepting groups has been demonstrated,[139] but the sulfilimines formed in this case undergo further reactions as a result of the imino-ylide tautomerism.

$$X_2CH{-}\underset{\underset{NR}{\|}}{S}Ar \rightleftharpoons X_2C{=}\underset{\underset{NHR}{|}}{S}Ar \longrightarrow X_2\underset{\underset{NHR}{|}}{C}{-}SAr$$

X = PhCO, MeCO; Ar = 2(4)-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$;
R = $PhSO_2$, 4-$MeC_6H_4SO_2$.

The use of sodium salts of sulfides instead of the sulfides themselves promotes the arenesulfonylimination of these compounds in an anionic form and also the stabilisation of the resulting *N*-arenesulfonylsulfilimino-anions.[47,121,131,133–136]

$$\left[\begin{matrix}X\\ Y\end{matrix}\!\!>\!C{=}{=}SR\right]^{-}Na^{+} + ArSO_2NNaCl \xrightarrow[-NaCl]{} \left[\begin{matrix}X\\ Y\end{matrix}\!\!>\!C{=}{=}\underset{\underset{NSO_2Ar}{\|}}{S}R\right]^{-}Na^{+}$$

R = 2(4)-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$;
X = Y = PhCO, MeCO, CN, EtOCO; X = MeCO, Y = EtOCO;
X = NO_2; Y = H, $PhCH_2$, PhCO, 2-$NO_2C_6H_4$.

Other *N*-chloro-compounds such as chloroamine, carboxylic acids *N*-chloroamides, *N*-chlorourethanes, *N*-chloroamidines, and *N*-chlorourea and its derivatives react with dialkyl and alkyl aryl sulfides to form aminosulfonium salts, which are converted into the corresponding sulfilimines on treatment with bases.[121]

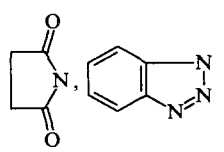
$$R_2S + XNHZ \longrightarrow R_2\overset{+}{S}NHZ\ X^- \xrightarrow[-HX]{HB} R_2S{=}NZ$$

R = Alk, Ar; X = Cl, Br;
Z = H, Alk, Ar, Het, AlkCO, ArCO, EtOCO,
RN=CR, NH_2—N=CH, NH_2CO.

Chlorine,[137] *tert*-butyl hypochlorite,[138–140] sulfuryl chloride,[121] *N*-chlorosuccinimide,[141–143] and other *N*-chloro-compounds,[137] the reactions of which with sulfides at low temperatures afford chlorosulfonium intermediates which are converted into sulfilimines by treatment with *N*-nucleophiles, are also used as sources of the chlorine cation.

$$R_2S + ZCl \longrightarrow \left[R_2\overset{+}{S}{-}Z\right]\bar{C}l \xrightarrow{R^1NH_2}$$

$$\longrightarrow R_2\overset{+}{S}NHR^1\bar{C}l \xrightarrow[-HCl]{HB} R_2S{=}NR^1$$

R = Alk, Ar;
Z = Cl, Bu^tO, SO_2Cl_2, 

Aliphatic, aromatic, and heterocyclic amines, *N*-aminophthalimide, cyanamide, and the sodioamides of sulfonic and carboxylic acids are used as the *N*-nucleophiles.[121]

The oxidative imination of sulfides by hydroxyaminosulfonic acid[121] is a special case of the general reaction involving the imination of sulfides by derivatives of hydroxylamine, in particular by *N*-arenesulfonyl-*O*-*p* nitrobenzenesulfonylhydroxylamine, *N*-ethoxycarbonyl-*O*-*p*-nitrobenzenesulfonylhydroxylamine, and *O*-mesitylenesulfonylhydroxylamine.

$$R_2S + XYNOY \longrightarrow R_2\overset{+}{S}NH(X)\bar{O}Y \xrightarrow[-HOY]{HB} R_2S{=}NX$$

R = Alk, Ar;
X = H, $ArSO_2$, EtOCO;
Y = HSO_3, 2,4,6-$Me_3C_6H_2SO_2$, 4-$NO_2C_6H_4SO_2$.

Sulfilimines are also formed in the reaction of sulfides with nitrenes generated by photochemical, thermal, and chemical methods. The procedure involving the photolysis of various organic azides in the presence of an excess of the sulfide has come to be most widely used.

$$XN_3 \xrightarrow{h\nu} :NX \xrightarrow{R_2S} R_2S{=}NX$$

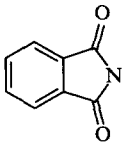
X = $ArSO_2$, PhCO, EtOCO, R_2PO;
R = Alk, Ar.

The reaction has been studied for a series of arenesulfonyl,[144] acyl,[121] alkoxycarbonyl,[121,144] diphenylphosphonyl, and dialkylphosphonyl azides.[145] It has been noted[121] that sulfides react with singlet nitrenes faster than with triplet nitrenes, since the presence in the reaction mixture of substances inducing the formation of triplet nitrenes inhibits the formation of sulfilimines. The low yields of the latter may be caused by their chemical instability. Under the conditions of photolysis, the sulfilimines are themselves sources of nitrenes, which has been noted[121] in the case of the photolysis of *N*-ethoxycarbonyl-*S*-*S*-dimethylsulfilimine. Certain unstable heterocyclic compounds, the photolysis of which in the presence of sulfides leads to the formation of sulfilimines, also function as sources of nitrenes.

$$Ph{-}\underset{\underset{O}{\|}}{\overset{N{-}O}{C}}{-}\underset{\underset{O}{|}}{C}{=}O + Me_2S \xrightarrow{h\nu} Me_2S{=}NCOPh + CO_2$$

The main disadvantage of the methods of synthesis of sulfilimines by the reaction of sulfides with thermally generated nitrenes is the thermal instability of the sulfilimines formed, for example, in the thermolysis of acyl azides,[146] alkoxycarbonyl azides, and arenesulfonyl azides in the presence of sulfides.[146,147] In the presence of copper, the thermolysis of the azides and hence the interaction of nitrenes with sulfides proceed at a lower temperature, which promotes a higher yield of sulfilimines.[148] The chemical synthesis of nitrenes with the aim of obtaining sulfilimines is more rarely employed. The synthesis of certain sulfilimines by the reaction of sulfides with arenesulfonamides and *N*-aminophthalimide in the presence of lead tetraacetate has been described.[121]

$$R_2S + NH_2X \xrightarrow{Pb(OAc)_4} R_2S{=}NX$$

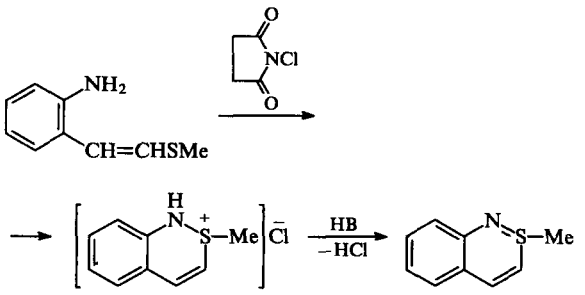
X = $ArSO_2$, 

One cannot rule out the possibility that the formation of sulfilimines in the reactions of sulfides with compounds having an E=N bond (E = S, I), which has been described in the literature,[149,150] also proceeds via a nitrene generation stage.

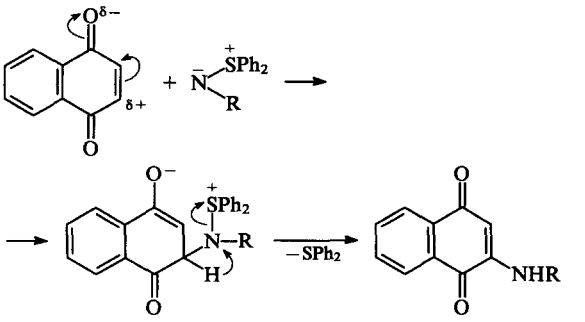
$$R_2S + X{=}NTs \longrightarrow R_2S{=}NTs$$

X = TsN =S, ArI.

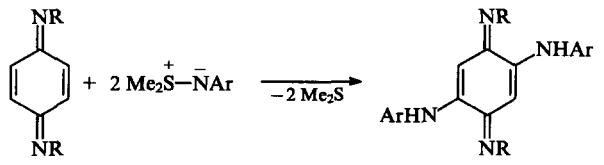
It has been shown[151] that, on treatment with *N*-chlorosuccinimide, aromatic amines containing an alkylthio-group in the *ortho*-position give rise to cyclic aminosulfonium salts, which are converted into cyclic sulfilimines in the presence of bases.



The conversion of sulfides into sulfilimines is of great synthetic importance, since the latter possess a series of valuable properties used in organic syntheses. Some of these syntheses are accompanied by the regeneration of the initial sulfides. For example, the high nucleophilicity of the nitrogen in *N*-arenesulfilimines makes it possible to use them for the introduction of aryl amino-groups into the quinonoid ring of quinone imines with regeneration of the initial sulfide.[121,152]

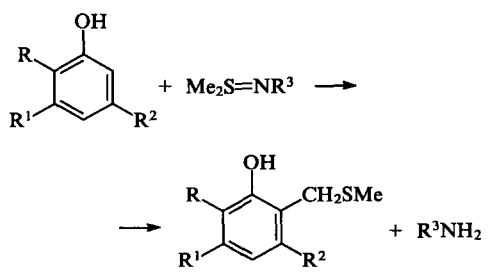


R = $PhCH_2$.



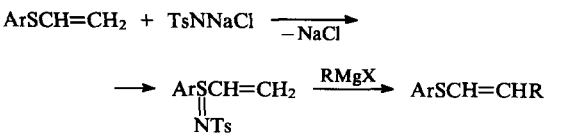
R = $PhSO_2$, *p*-$MeC_6H_4SO_2$;
Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-$NO_2C_6H_4$.

S,S-Dimethylsulfilimines are used to introduce the methylthiomethylene group into the aromatic ring of phenols.[121]



R = Me, OMe; R^1 = H, Me; R^2 = $ArSO_2$; 2,4-$(NO_2)_2C_6H_3$.

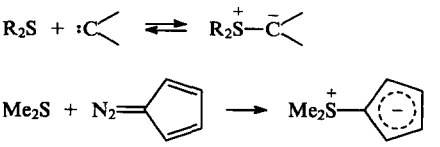
Substituents can also be introduced into vinyl sulfides $ArSCH=CH_2$ via the sulfilimine formation stage, whereupon the compounds ArSCH=CHR are formed.[8]



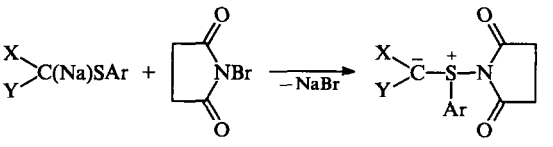
S-Alkyl-*S*-allyl-*N*-tosylsulfilimines cyclise intramolecularly on treatment with NaOH, affording 2-vinyl-substituted cyclic amines.[153]

c. The formation of sulfur ylides

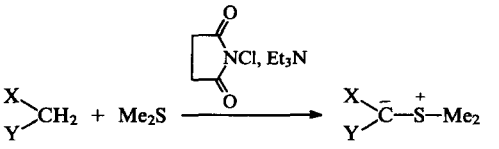
The interaction of sulfides with carbenes leads to sulfur ylides, which are not always stable and can undergo various rearrangements.[7]



The formation of relatively stable sulfur ylides on interaction of the sodium salts of α-arylthio-derivatives of CH acids with *N*-bromosuccinimide in acetone[154] and also on interaction of dimethyl sulfide and *N*-chlorosuccinimide with CH acids in the presence of triethylamine[155] has been noted.

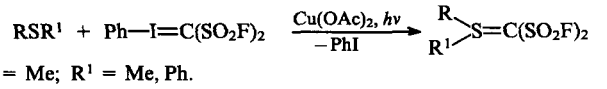


X = MeCO, Y = EtOCO; X = $PhSO_2$, Y = Ph;
Ar = 2-$NO_2C_6H_4$, 4-$NO_2C_6H_4$.



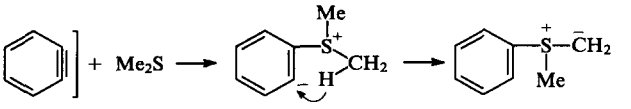
X = Br, Ac, CN, $PhCH_2$; Y = Br, $EtCO_2$, $MeCO_2$, Ph.

The thermal and photochemical decomposition of phenyliodonium bis(fluorosulfonyl)methylides in the presence of sulfides leads to the formation of relatively stable sulfur ylides.[156]

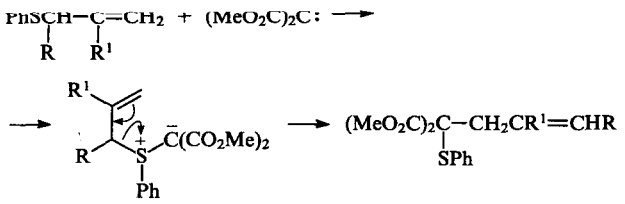


R = Me; R^1 = Me, Ph.

The addition of sulfides to dehydrobenzene also affords relatively stable sulfur ylides.[8]

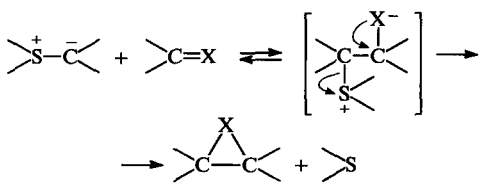


The insertion of carbenes in the allylic C–S bond[8,157] proceeds via the formation of ylides.



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

Sulfur ylides are used widely in organic synthesis for the transfer of the alkylidene group to an electrophilic double bond with formation of a three-membered ring.[121]

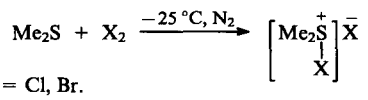


X = O, C.

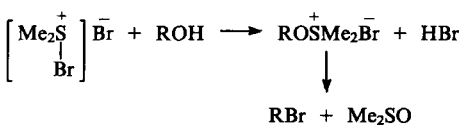
It has been suggested[8] that the biosynthesis of the cyclopropane ring in a number of natural products proceeds via the copper-catalysed transfer of the methylene group of the ylide formed from *S*-adenosylmethionine.

d. The formation of halosulfonium halides and other sulfonium salts

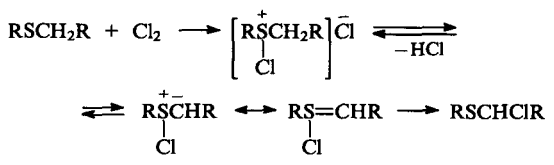
Dimethyl sulfide reacts with Cl_2 or Br_2 at −25 °C in $CHCl_3$ to form charge-transfer complexes or halodimethylsulfonium halides and is used in organic synthesis to convert alcohols into alkyl halides.[7]



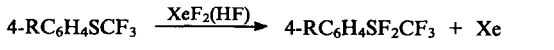
X = Cl, Br.



Chlorosulfonium chlorides are intermediates in the α-chlorination of sulfides.[7]

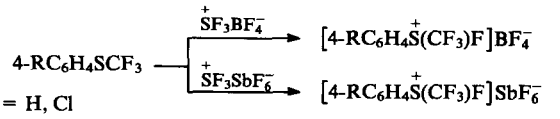


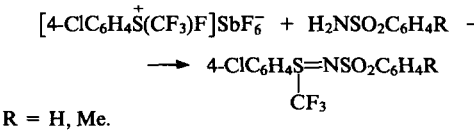
Aryl trifluoromethyl sulfides do not react with chlorine or bromine, but, on treatment with xenon fluoride, they combine with two fluorine atoms, affording readily hydrolysable aryldifluoro(trifluoromethyl)sulfuranes in a quantitative yield.[4]



R = H, Cl, NO_2.

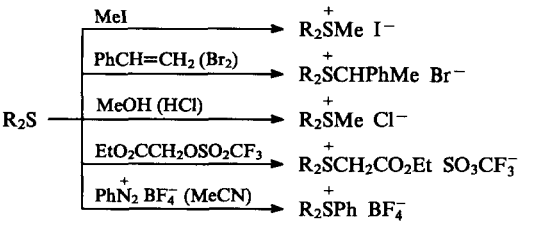
Treatment of aryl trifluoromethyl sulfides with the complexes $SF_3^+BF_4^-$ and $SF_3^+SbF_6^-$ yields arylfluoro(trifluoromethyl)-sulfonium salts,[158] which are used in the synthesis of *N*-arenesulfonyl-*S*-aryl-*S*-trifluoromethylsulfilimines.[4]



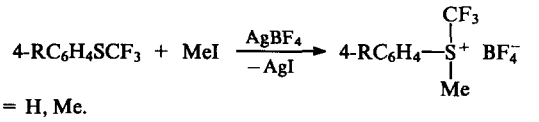


R = H, Me.

The interaction of sulfides with electrophiles or reagents capable of forming cationoid species results in the formation of sulfonium salts, which remain unchanged under the reaction conditions only in rare cases. The reaction involving the alkylation (arylation) of sulfides by alkyl halides, alkenes, alcohols, trifluoromethanesulfonates, and diazonium salts is usually employed to obtain sulfonium salts in a pure form.

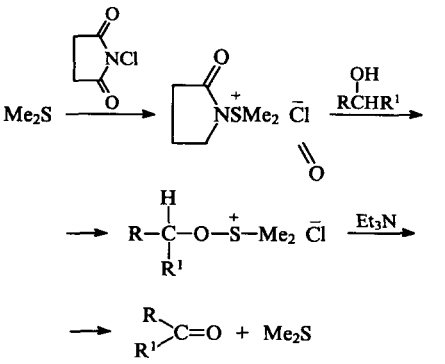


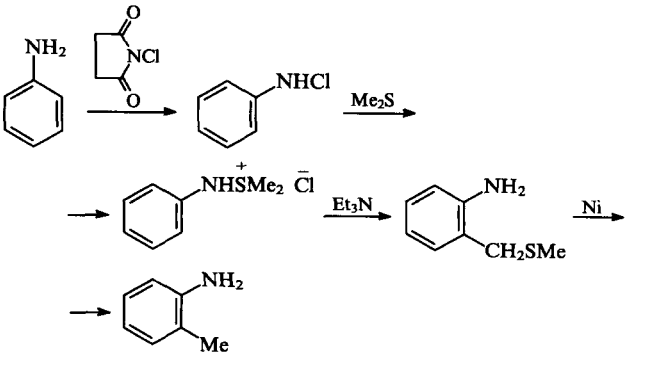
Despite the low nucleophilicity of the sulfur atom, aryl trifluoromethyl sulfides are alkylated by methyl iodide in the presence of $AgBF_4$.[4]



R = H, Me.

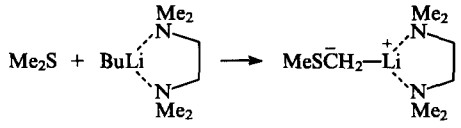
Aminosulfonium salts, used to oxidise alcohols and to *ortho*-methylate anilines, are formed on interaction of sulfides with *N*-chlorosuccinimide and also with amines in the presence of *N*-chlorosuccinimide.[121]





2. Generation of α-sulfenylcarbanions

Sulfides containing a mobile α-H atom relatively easily form carbanions in the stabilisation of which the sulfur atom is directly involved.[159] Depending on the acidity of such sulfides, sodium methoxide,[131–136] potassium *tert*-butoxide,[160] alkali metal hydroxides,[161–163] sodium hydride,[167] and *tert*-butyllithium in THF[16] are used to synthesise carbanions. For example, dimethyl sulfide forms a carbanion on reaction with the butyllithium–tetramethylethylenediamine (TMEDA) complex.[16]



Methyl phenyl sulfide is converted into phenylthiomethyllithium on treatment with butyllithium in the presence of diazabicyclo[2.2.2]octane (DABCO).[16]

Reactions involving the substitution by a metal of atoms and groups such as Br, $SnBu_3$ and SePh as well as reactions involving the addition of organometallic reagents to the C=C bond of vinyl sulfides and to the C=S bonds of thioketones are much more rarely used in the synthesis of α-sulfenylcarbanions.[16,165]

The stability of the α-C-anionic centre increases following the enhancement of the *s* character of the carbon atom and also with increase in the number of sulfenyl groups linked directly to this atom, which is clearly confirmed by the comparison of the pK_a of the following compounds: PhSMe (49), $(PhS)_2CH_2$ (30.8), and $(PhS)_3CH$ (22.8).[166] The stability of the α-C-anionic centre is also influenced by other factors, in particular by the presence of neighbouring electron-accepting groups and atoms participating in the delocalisation of the negative charge,[47–51,167] the possibility of the transfer of the negative charge to other atoms as a result of tautomerism or isomerisation,[131,135] and also the possibility of the stabilisation of the counterion as a result of chelate formation.[16]

The question of the mechanism of the stabilisation of the α-C-anionic centre by a divalent sulfur atom has not so far been ultimately elucidated and still remains controversial. There are several concepts which explain the ability of sulfur to stabilise the α-C-anionic centre. According to one of them,[7] the α-C-anionic centre is stabilised by the sulfur atom as a result of the transfer of electrons from the carbanionic centre to the *d* orbitals of the sulfur atom. Despite the fact that doubts have been repeatedly cast on this concept, nevertheless investigators still prefer to resort to it even in recent years.[47,131–135]

According to another concept, the α-C-anionic centre is stabilised by the sulfur atom as a result of the dispersion of the negative charge owing to the more ready polarisability of the electron cloud of the sulfur atom compared with the carbon atom.[16] The polarisabilities of the sulfur and carbon atoms are 3.8×10^{40} and 1.9×10^{40} C m^2 V^{-1}, while the values for the C–S and C–C bonds are 2.1×10^{40} and 1.1×10^{40} C m^2 V^{-1} respectively.[16]

The concept of η,σ^*-delocalisation (hyperconjugation) has also been proposed, in satisfactory agreement with X-ray diffraction data for the lithio-derivatives of dimethyl sulfide, methyl phenyl sulfide, 1,3-dithiane, and 2-phenyl-1,3-dithiane as well as ^{13}C and ^6Li NMR spectrometric data.[16]

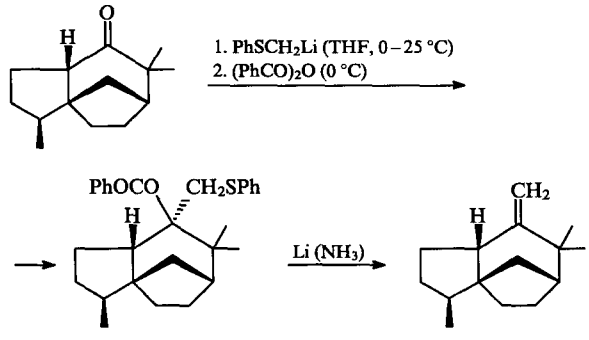
In studying the reactivity of α-sulfenylcarbanions and the reactions involving them, it is necessary to begin with the fact that α-sulfenylcarbanions are in essence ambident anions and their reactions with electrophiles proceed either via the carbon atom or the sulfur atom depending on the nature of the electrophile. By exerting its stabilising influence on the α-C-anionic centre, the divalent sulfur atom undergoes an increase in its electron density owing to the displacement of the latter from the anionic centre, which has been confirmed by quantum-mechanical calculations.[131] As a result of such increase in electron density, the sulfur atom becomes more susceptible to attack by the electrophile.

Examples of the reactions of α-sulfenylcarbanions with electrophiles involving the participation of the carbon atom are provided by the *C*-alkylation[16,47] and *C*-acylation[47] reactions and also by the reactions involving the addition of the α-C-anionic centre to the electron-deficient carbon atom of the carbonyl group.[161–163] In view of the possibility of the subsequent elimination of the sulfenyl group, these reactions play a major role in fine organic synthesis and, in particular, in the formation of the C–C and C=C bonds in the synthesis of various natural products. The formation of higher homologues of alkyl iodides[168] and the synthesis of the sesquiterpene zizaene may be quoted as clear-cut examples.[169]

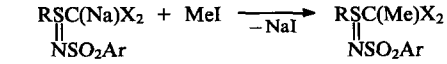
The formation of higher homologues of alkyl iodides involves the alkylation of phenylthiomethyllithium by an alkyl iodide and subsequent replacement of the phenylthio-group by iodine on treatment with methyl iodide in the presence of sodium iodide. Ultimately one obtains an alkyl iodide containing one or several carbon atoms more than the initial compound.



The synthesis of the sesquiterpene zizaene consists in the addition of phenylthiomethyllithium to the carbonyl group of a cyclic ketone and subsequent benzoylation of the resulting β-hydroxysulfide and the reductive elimination of the phenylthio-group with the aid of lithium in liquid ammonia.



The reactions of α-sulfenylcarbanions with electrophiles involving the sulfur atom were discovered comparatively recently. They include the reactions of the sodium salts of sulfides with *N*-halo-derivatives and in particular the oxidative imination[47,131,134,135] and oxidative imidation[154] of the sodium salts of sulfides, which were considered in the previous Section. The primary step in these reactions is attack on the positively charged halogen atom of the *N*-halo-compound by the sulfur atom with formation of a halosulfonium intermediate,[121] which reacts with the *N*-anion to form the reaction product. The sodium salts of *N*-arenesulfonylsulfilimines, synthesised by the arenesulfonylimination of the sodium salts of sulfides, readily undergo *C*-alkylation,[131,135] which is very important for the synthesis of new *N*-arenesulfonylsulfilimines.



R = 2(4)-$NO_2C_6H_4$; X = MeCO, EtOCO; Ar = 4-MeC_6H_4.

3. Reactions involving the cleavage of the C–S bond

The C–S bond is cleaved comparatively readily compared with the C–C bond or a nonactivated C–H bond under the influence of heat or chemical reagents. For example, the pyrolysis of benzyl phenyl sulfide in cyclohexane begins already at 200 °C with the homolytic cleavage of the C–S bond.[170] The composition of the products of the pyrolysis of sulfides is then determined both by the structure of the initial sulfide and by the pyrolysis conditions.

For example, in the gas phase at 400–800 °C diethyl sulfide decomposes to hydrogen sulfide and ethylene, which are formed as a result of the following reactions.[171]

$$CH_3CH_2SCH_2CH_3 \xrightarrow{\Delta} CH_3CH_2\dot{S} + CH_3\dot{C}H_2$$

$$CH_3\dot{C}H_2 + CH_3CH_2SCH_2CH_3 \longrightarrow$$

$$\longrightarrow CH_3CH_3 + CH_3CH_2S\dot{C}HCH_3$$

$$CH_3CH_2S\dot{C}HCH_3 \longrightarrow CH_3CH_2\dot{S} + CH_2{=}CH_2$$

$$CH_3CH_2\dot{S} + CH_3\dot{C}H_2 \longrightarrow CH_3CH_2SH + CH_2{=}CH_2$$

$$CH_3CH_2SH \longrightarrow H_2S + CH_2{=}CH_2$$

The formation of hydrogen sulfide and the corresponding alkenes has been observed[172] also in the thermolysis of other dialkyl sulfides. Under these conditions, dialkyl sulfides with the iso-structure and asymmetric dialkyl sulfides are thermally less stable than symmetrical sulfides with the normal structure. The pyrolysis of allyl methyl sulfide at 427 °C leads to thioformaldehyde and propene.[173] Other alkyl allyl sulfides are converted into the corresponding thiocarbonyl compounds and alkenes under the conditions of vacuum pulse pyrolysis at 615–650 °C.

$$\rangle CH{-}S{-}CH_2{-}CH{=}CH_2 \longrightarrow \rangle C{=}S + MeCH{=}CH_2$$

Diallyl and allyl benzyl sulfides form thioacrolein and thiobenzaldehyde respectively under these conditions.[174] The vacuum pulse pyrolysis of allyl phenyl sulfide proceeds with formation of phenylthiyl and allyl radicals, which dimerise under the pyrolysis conditions.[172] The vacuum pyrolysis of alkyl ethynyl sulfides at 500 °C leads to the formation of thioketene.[16]

$$CH{\equiv}CSCMe_3 \xrightarrow{500\,^\circ C} [CH{\equiv}C\dot{S} + \dot{C}Me_3] \longrightarrow$$

$$\longrightarrow CH{\equiv}CSH + CH_2{=}CMe_2$$

$$CH{\equiv}CSH \longrightarrow CH_2{=}C{=}S$$

The products of the pyrolysis of the sulfide $PhCH_2CH(Ph)SPh$ at 250 °C are H_2S, PhMe, $PhCH_2CH_2Ph$, PhCH = CHPh, PhSH, Ph_2S, thianthrene, and 2,3,4,5-tetraphenylthiophene.[175]

The thermal disproportionation of alkyl sulfides in the presence of carboxylic acid esters is one of the transesterification methods.[8]

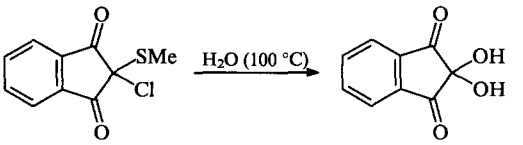
$$RCO_2Me + R^1SR^1 \xrightarrow{\Delta} RCO_2R^1 + R^1SMe$$

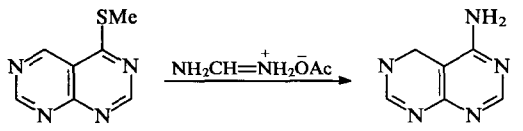
The dealkylation of butyl methyl sulfide in the presence of alkanechalcogenolate anions, which proceeds with formation of butanethiolate and methanethiolate anions in 40% and 35% yields respectively, has been described.[176] The thiolate anions react with propyl iodide, affording the corresponding sulfides.

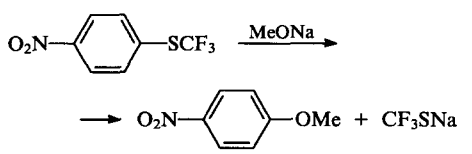
The reductive cleavage of sulfides, in which there is a clear tendency towards the preferential cleavage of one of the two C–S bonds, is used in the synthesis of thiols. The ease of the cleavage of the C–S bond diminishes in the sequence alkynyl > vinyl > allyl > alkyl.[78] Sodium in liquid ammonia or lithium in ethylamine are used for the reductive cleavage of allyl and benzyl sulfides. The reductive cleavage of 3-alkylthioindolenine to indole proceeds on treatment with $LiAlH_4$, Raney nickel in ethanol, or $NaBH_4$ in isopropyl alcohol. The reductive cleavage on treatment with CF_3COOH in the presence of a suitable nucleophilic trapping agent is also used.[177] One of the methods for the protection of the SH group involves its conversion into the sulfide group, which is as a rule achieved as a result of alkylation, acylation, or addition reactions. The protecting groups are removed by means of various methods for the cleavage of the C–S bond, using bases, acids, mercury acetate and sulfate, silver nitrate in pyridine, and trifluoromethanesulfonic acid, as well as electrolytic cleavage.[78]

The anodic[178] and oxidative[179] desulfurisation of cyclic dithioacetals by *N*-halo-compounds in the presence of sources of fluoride ions ($Bu_4N^+H_2F_3^-$, $Et_3N \cdot HF$) may be used as preparative methods of synthesis of geminal difluoroalkanes.

Certain sulfides undergo relatively easily hydrolysis, aminolysis, and alcoholysis with cleavage of the C–S bond.[4,8]







The sulfides in which the sulfur atom is linked to the benzyl or an acyl[180] group undergo chlorinolysis comparatively readily, which is frequently used in the synthesis of sulfenyl chlorides.

$$ArSCH_2Ph + Cl_2 \xrightarrow{CH_2Cl_2} ArSCl + PhCH_2Cl$$

$$RSAc + SO_2Cl_2 \xrightarrow{CCl_4} RSCl + AcCl + SO_2$$

R = Me, Bu, Bu^t, Ph, 2-MeC_6H_4, 4-$NO_2C_6H_4$.

Asymmetric sulfides are obtained by the cleavage of the C–S bond in symmetrical sulfides in the presence of iodonium[181] or sulfonium[182] salts.

$$Me_2S + [\overset{+}{I}C_6F_{13}]BF_4^- \longrightarrow$$

$$\longrightarrow [Me_2\overset{+}{S}C_6F_{13}]BF_4^- \xrightarrow{Me_2S} MeSC_6F_{13} + \overset{+}{S}Me_3\ BF_4^-$$

$$R_2CHBr + R^1_2S \longrightarrow$$

$$\longrightarrow \left[\begin{array}{l} R^1_2\overset{+}{S} \\ \quad | \\ \quad CHR_2 \end{array}\right] \bar{B}r \xrightarrow{R^1_2S} R_2CHSR^1 + R^1_3\overset{+}{S}\ \bar{B}r$$

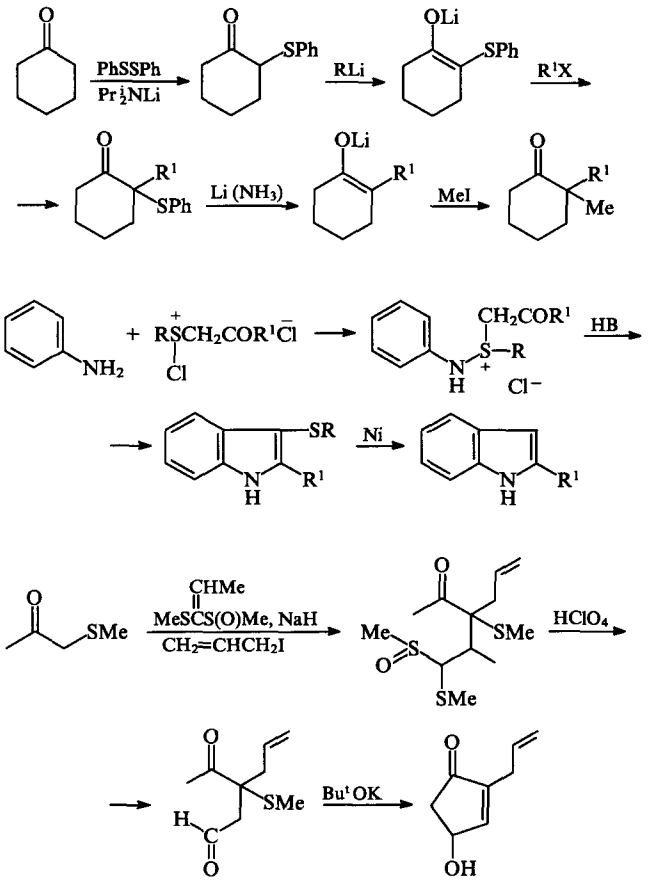
On treatment with bromocyanogen, the C–S bond in aliphatic sulfides is cleaved with formation of thiocyanates and alkyl bromides.[8] Asymmetric sulfides are then cleaved in such a way that the thiocyanate group is bound to the alkyl group.

$$BuSPr + BrCN \longrightarrow BuSCN + PrBr$$

The sulfides in which the sulfur atom is linked to the carbon atom in the β-position relative to unsaturated groups, for example to a carbonyl group or a benzene ring, very easily undergo elimination with cleavage of the C–S bond, which is catalysed by bases;[15] the driving factor in this case is the formation of a system of conjugated bonds.

$$O{=}\overset{|}{C}{-}\overset{|}{C}H{-}\overset{|}{C}{-}SR \xrightarrow{\bar{O}H} O{=}\overset{|}{C}{-}\overset{|}{C}{=}\overset{|}{C} + H_2O + RS^-$$

The elimination of alkylthio- and arylthio-groups has found extensive application in recent years in the syntheses of various cyclic compounds.[8]

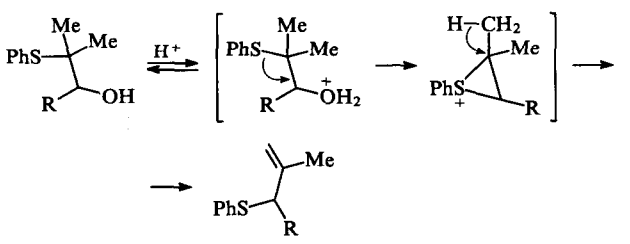


4. Rearrangements of sulfides

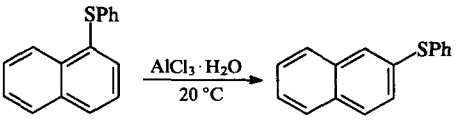
Among all the divalent sulfur compounds, sulfides show perhaps the greatest tendency towards various rearrangements in which the sulfur atom participates directly in the formation of transition states.[183] Sigmatropic rearrangements, which proceed with migration of σ-bonds via a transition state in which the sulfur atom is frequently involved, are characteristic of sulfides under these conditions. The theoretical possibility of the occurrence of a particular rearrangement in the series of sulfides is regulated by the selection rules for pericyclic reactions. In practice 1,2-, 2,3-, and 3,3-sigmatropic rearrangements are observed in the series of sulfides.

a. 1,2-Sigmatropic rearrangements

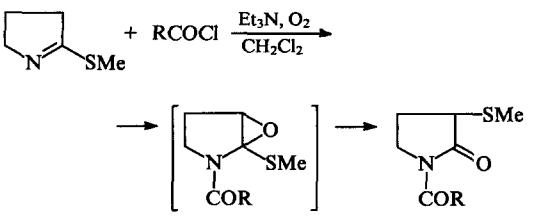
According to the correlation rules, the 1,2-migration of arylthio- and alkylthio-groups in the neutral molecules of sulfides is prohibited. It can occur either in a cation or on radical initiation.[183] Indeed, the 1,2-shift of the phenylthio-group, which occurs in aryl β-hydroxyalkyl sulfides on treatment with toluene-*p*-sulfonic acid, is due to the formation of a cationoid intermediate.[184]



The intramolecular 1,2-migration of the arylthio-group in the molecule of 1-naphthyl phenyl sulfide in the presence of aluminium chloride also evidently proceeds via the stage involving the formation of a cationoid intermediate.[183]

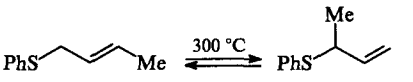


The *N*-acylation of 2-methylthiodihydropyrroline, in which the initial compound is epoxidised by atmospheric oxygen with subsequent opening of the epoxide ring and the migration of the methylthio-group to the 3-position, may be quoted as an example of the 1,2-migration of the methylthio-group.[185]

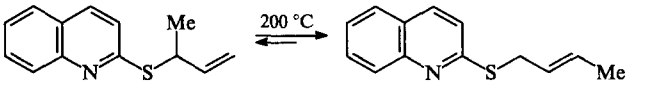


b. 1,3-Sigmatropic rearrangements

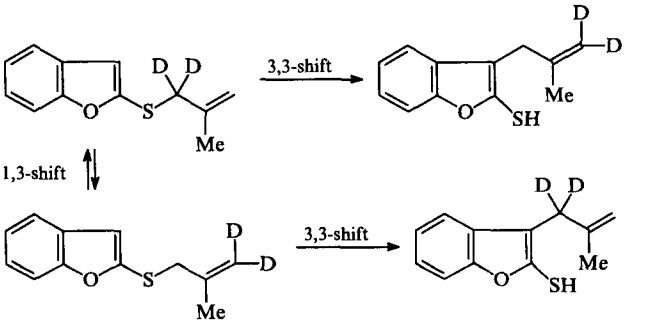
1,3-Sigmatropic rearrangements are characteristic primarily of allyl sulfides. For example, 2-butenyl phenyl sulfide is converted into 1-methylallyl phenyl sulfide at 300 °C as a result of the 1,3-migration of the phenylthio-group.[183]



The 1,3-sigmatropic rearrangement of 1-methylallyl 2-quinolinyl sulfide is a reversible reaction the equilibrium in which at 200 °C is appreciably displaced towards the formation of 2-butenyl 2-quinolinyl sulfide.[183]



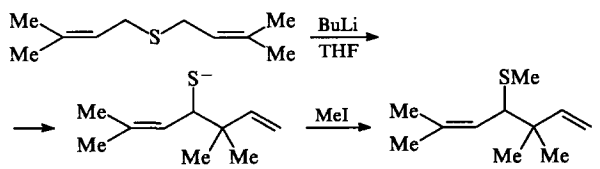
In a number of instances, the 1,3-sigmatropic rearrangement of sulfides is accompanied by their subsequent 3,3-sigmatropic rearrangement. Thus, the 1,3-sigmatropic rearrangement of the deuterium-labelled 2-benzofuryl 2-methylallyl sulfide is accompanied by the 3,3-sigmatropic rearrangement, which occurs at a higher temperature.[186–188]

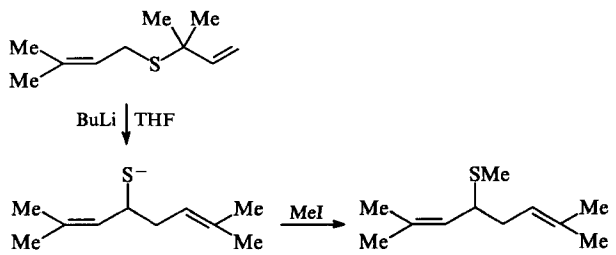


This behaviour is observed most frequently in the 1,3-sigmatropic rearrangement of allyl phenyl sulfide and allyl 2-thienyl sulfide.[187,188] The 1,3-sigmatropic rearrangement of allyl aryl sulfides is accelerated by singlet oxygen obtained photochemically or on decomposition of peroxides.[189] Diaryl sulfides also exhibit an accelerating effect on the 1,3-sigmatropic rearrangement of allyl aryl sulfides.[190]

c. 2,3-Sigmatropic rearrangement

The 2,3-sigmatropic rearrangements of sulfides proceed as a rule under the influence of basic catalysts with formation of α-sulfenylcarbanions as intermediates. The possibility of the 2,3-sigmatropic rearrangement is then determined by the structure of the initial sulfide and the nature of the catalyst and the solvent. For example, on treatment with butyllithium in THF, diallyl sulfides undergo the 2,3-sigmatropic rearrangement with formation of the corresponding thiolates, which react with methyl iodide, affording dienyl methyl sulfides.[183–191]





In the DMSO – KOH system, diallyl sulfide merely isomerises to di(1-propenyl) sulfide.[192]

$$CH_2{=}CH{-}CH_2SCH_2{-}CH{=}CH_2 \xrightarrow{DMSO/KOH} CH_3{-}CH{=}CHSCH{=}CH{-}CH_3$$

Treatment of allyl benzyl sulfide with butyllithium in the presence of diaza-1,4-bicyclo[2.2.2]octane and methyl iodide at −15 °C leads to the formation of a mixture of three sulfides.[193]

$$PhCH_2SCH_2CH{=}CH_2 \xrightarrow[MeI]{BuLi,\ DABCO} \begin{cases} PhCH(SMe)CH_2CH{=}CH_2 & 23\% \\ PhCH_2SCH(Me){=}CH_2 & 76\% \\ PhCH_2SCH{=}CHCH_2Me & 1\% \end{cases}$$

These results indicate the formation of two intermediate carbanions — with the negative charge on the benzyl and allyl carbon atoms. The carbanion with the negative charge on the benzyl carbon atom undergoes a 2,3-sigmatropic rearrangement whereas the carbanion with the negative charge on the allyl carbon atom is stable; it is merely methylated by methyl iodide and isomerises with migration of the double bond.

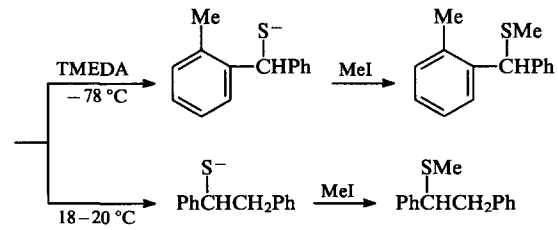
The 2,3-sigmatropic rearrangement of benzyl γ,γ-dimethylallyl sulfide under similar conditions leads to only one product.

$$PhCH_2SCH_2{-}CH{=}C(Me)(Me) \xrightarrow[2.\ MeI]{1.\ BuLi,\ DABCO} Ph{-}CH(SMe){-}C(Me)(Me){-}CH{=}CH_2$$

It has been suggested[183] that in this case only the carbanion with the negative charge on the benzyl carbon atom is involved in the 2,3-sigmatropic rearrangement, whereas the carbanion with the negative charge on the allyl carbon atom does not participate in the rearrangement and other reactions.

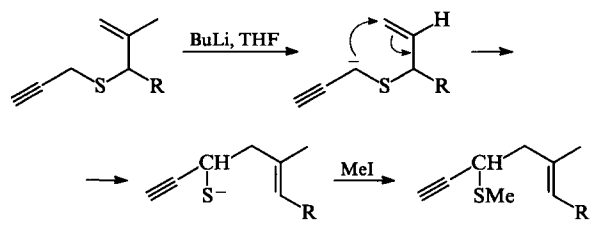
Depending on the conditions, the carbanion of dibenzyl sulfide can undergo the Stevens rearrangement or the 2,3-sigmatropic rearrangement.[193]

$$PhCH_2SCH_2Ph \xrightarrow{BuLi} PhCHSCH_2Ph \longrightarrow$$

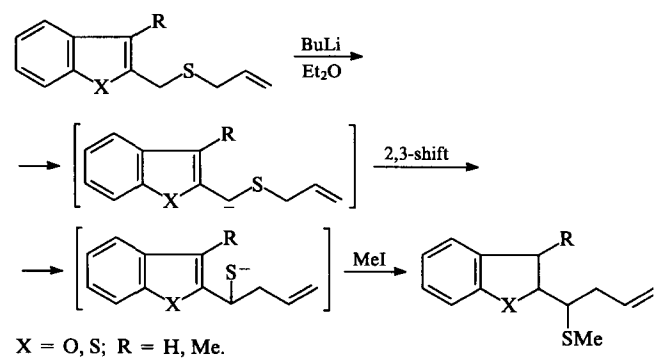


Since the Stevens rearrangement proceeds in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), it has been suggested[193] that the 2,3-sigmatropic rearrangement occurs in the presence of free anions. On the other hand, if the anion is solvated, the Stevens rearrangement takes place.

Sulfides containing the propargyl group also undergo the 2,3-sigmatropic rearrangement on treatment with butyllithium in THF.[183]

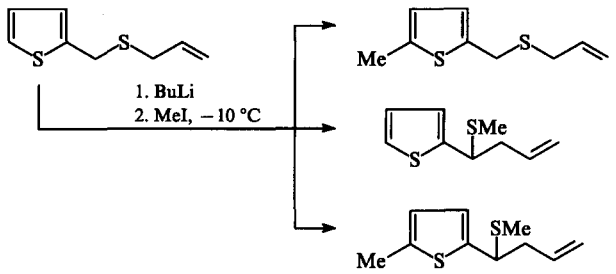


The possibility of the 2,3-sigmatropic rearrangement in the series of allyl heteroaryl sulfides is determined by the nature of the heteroaryl group.[194] For example, on treatment with butyllithium in diethyl ether at −70 °C, 2-(allylthiomethyl)benzofuran and 2-(allylthiomethyl)-3-methylbenzothiophene undergo the 2,3-sigmatropic rearrangement, affording the corresponding thiols, which give rise to sulfides on interaction with methyl iodide.

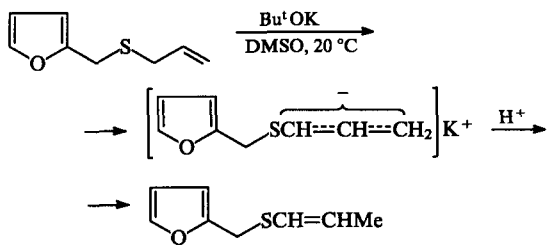


X = O, S; R = H, Me.

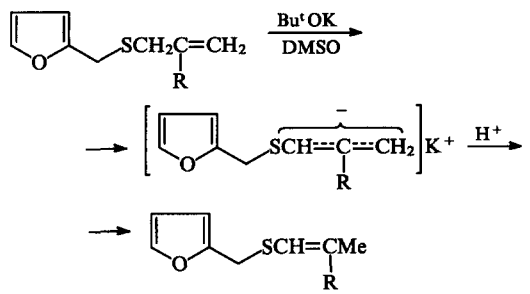
Under the same conditions, 2-(allylthiomethyl)thiophene remains unchanged and produces a mixture of sulfides only at −10 °C. Among these, the last two are the products of the 2,3-sigmatropic rearrangement of the initial sulfide.



The interaction of 2-(allylthiomethyl)furan with butyllithium leads to the metallation of the free α-position of the heterocycle. The replacement of butyllithium by potassium *tert*-butoxide leads to the selective formation of 2-(propenylthiomethyl)furan.

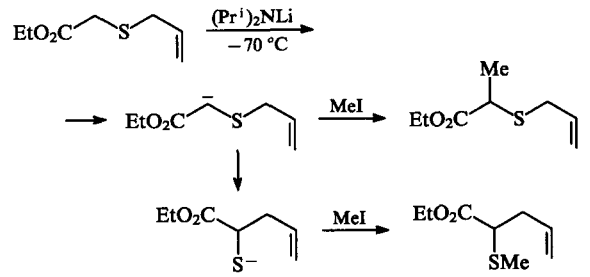


Other allyl furylmethyl sulfides undergo a similar isomerisation.[286]

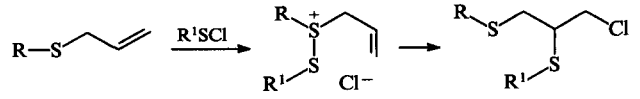


R = H, Me.

The 2,3-sigmatropic rearrangement of allyl ethoxycarbonylmethyl sulfide takes place in the presence of lithium diisopropylamide.[195]



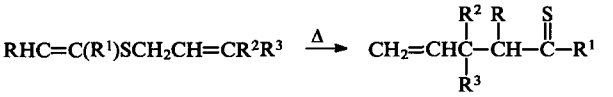
It has been suggested[196] that the products of the reactions of allyl sulfides with sulfenyl chlorides are formed not as a result of the addition of the sulfenyl chlorides to the allyl fragment but as a result of the 2,3-sigmatropic rearrangement of the sulfonium cation produced due to the attack by the sulfenyl chloride on the sulfur atom.



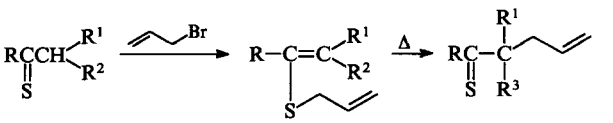
R = R¹ = Me.

d. The 3,3-sigmatropic rearrangement

The 3,3-sigmatropic rearrangement is characteristic primarily of allyl sulfides. The structure of the initial sulfide exerts a significant influence in this instance both on the rate of the rearrangement and on the nature of the product formed. The sulfides $RCH=C(R^1)SCH_2CH=CR^2R^3$ (R = H, Alk, Ph; $R^1 = NMe_2$, NEt_2, OEt, SEt; $R^2 = R^3$ = H, Me), for example, rearrange to the corresponding thiones even on slight heating.[183]



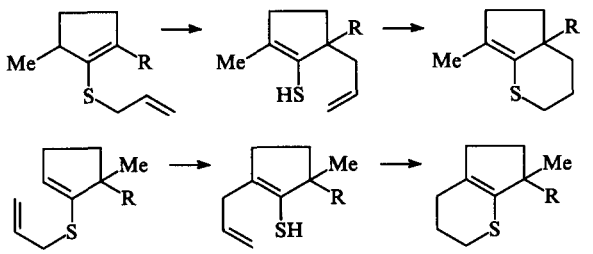
Substituted allyl vinyl sulfides, formed in the reactions of aliphatic thioketones with allyl bromides, undergo the 3,3-sigmatropic rearrangement even on distillation, affording thioketones.[183,197]



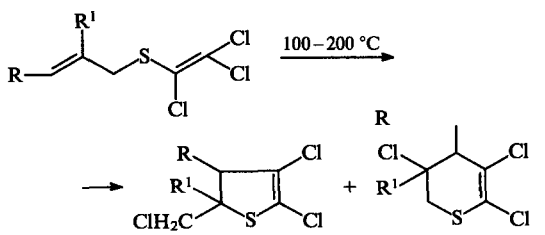
R = R¹ = R² = H, Me, Pr^i, Bu^t.

The presence of electron-accepting groups such as the nitrile group in the molecules of allyl vinyl sulfides hinders the 3,3-sigmatropic rearrangement. For example, dicyano-substituted allyl vinyl sulfides are converted into the isomeric ketones only after prolonged heating.

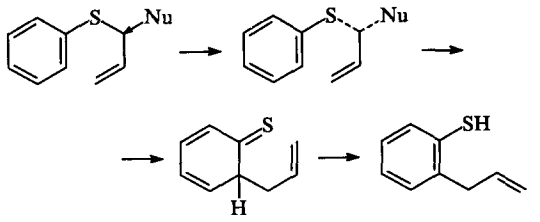
If one of the double bonds in allyl vinyl sulfides is part of an alicyclic system, the rearrangement results in the formation of enethiols, which slowly cyclise even at room temperature to the corresponding bicyclic sulfur-containing compounds.[183]



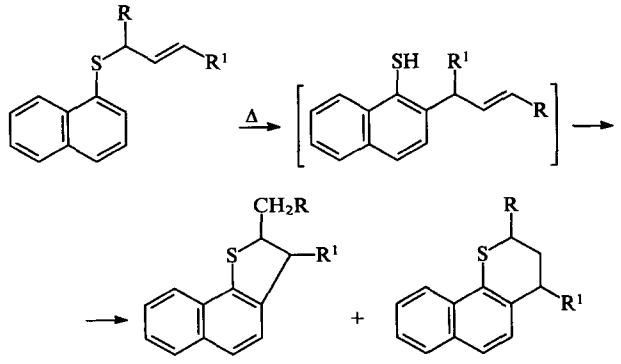
The thermal rearrangement of trichloro-substituted allyl vinyl sulfides involves the migration of the chlorine atoms, which results in the formation of chloro-substituted dihydrothiophenes and dihydrothiopyrans.[198]



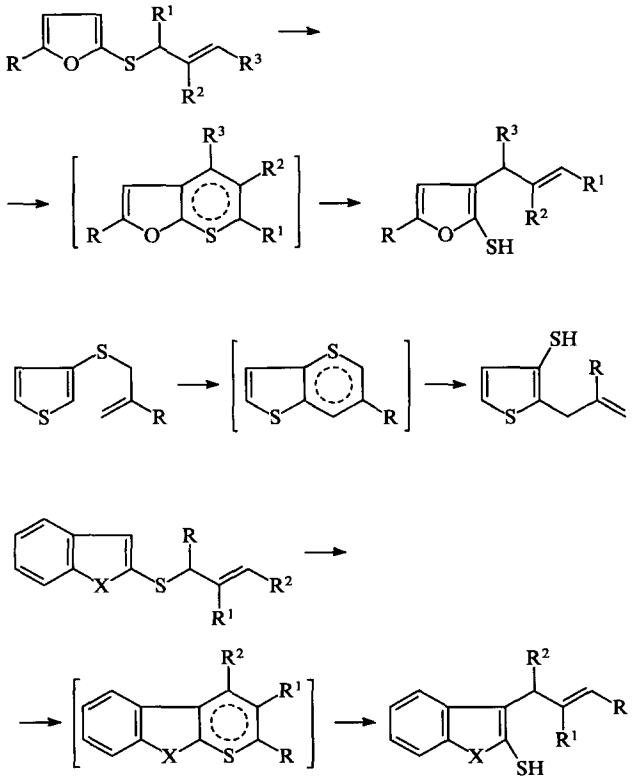
On distillation in the presence of quinoline and *N*,*N*-dimethylaniline, allyl phenyl sulfide rearranges to 2-allylthiophenol, which is converted under the reaction conditions into 2-methyl-2,3-dihydrobenzothiophene and other products. The study of this reaction provided Kwart et al.[199] with a basis which they used to put forward a mechanism of the nucleophilic catalysis with participation of solvent molecules.



Allyl 1-naphthyl sulfides rearrange similarly to allylnaphthalenethiols, which cyclise under the reaction conditions to 2,3-dihydronaphtho[1,2-*b*]thiophenes and 2,3-dihydronaphtho[1,2-*b*]thiopyrans.[188,200]

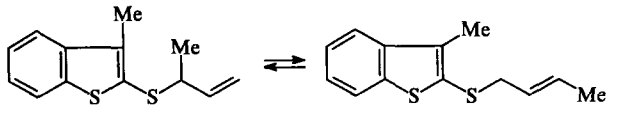


On heating in the absence of a solvent, substituted allyl furyl and allyl thienyl sulfides and their benzo-derivatives undergo a 3,3-sigmatropic rearrangement with formation of allyl-substituted heterocyclic thiols.[201–208]



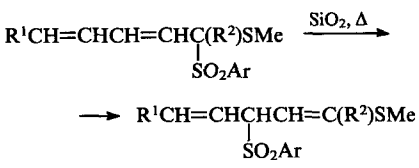
X = O, S; R = R¹ = R² = R³ = H, Me, MeO, MeS, Cl, Br.

It has been noted[187,204] that the 3,3-sigmatropic rearrangement of alkenyl heteroaryl sulfides is as a rule accompanied by the 1,3-sigmatropic shift and this course of the reaction is virtually the only one for allyl benzothienyl sulfides containing a substituent in the 3-position in the thiophene ring.[206]



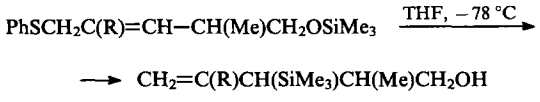
The replacement of the double bond in the allyl or vinyl fragments of allyl vinyl sulfide by a triple bond hardly affects the mode of the 3,3-sigmatropic rearrangement. The products of the 3,3-sigmatropic rearrangements of sulfides with a triple bond are also thiols, thiones, and cyclic compounds with the sulfur atom in the heterocycle.[183]

Among other rearrangements of unsaturated sulfides, mention should be made of the rearrangements of phenylthioacetylene, which is converted into 1,2-di(phenylthio)ethylene in the DMSO–KOH system[209] and also the rearrangement of allyl sulfides containing an arenesulfonyl group at the allylic carbon atom, which proceeds with migration of the arenesulfonyl group.[210]



R^1 = H, Et; R^2 = Et, $PhCH_2$; Ar = Ph, 4-MeC_6H_4.

The rearrangement of allyl sulfides containing the trimethylsiloxane group has been described.[211] The rearrangement takes place in the presence of di-*tert*-butylbiphenylyllithium with migration of the trimethylsilyl group, which results in the formation of allylsilanes with a high regioselectivity and stereoselectivity.



R = H, Me.

* * *

It is seen from the present review that studies in the field of the chemistry of sulfides during the last ten years have been directed mainly to the further development of the methods of synthesis of sulfides already available such as the sulfenylation of hydrocarbons, the alkylation of thiols, and the thiylation of unsaturated compounds, as well as to the search for new methods of synthesis (aminosulfenylation and sulfamatosulfenylation of olefins, etc.). Much attention has been devoted to further study of the reactivity of sulfides and in particular of the reactions occurring with formation of halosulfonium intermediates, α-sulfenylcarbanions, and sulfur ylides, as well as rearrangements. Many investigations have been devoted to syntheses based on sulfides.

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