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Thiols as synthons

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Abstract. The results of recent research in the field of thiol chemistry are arranged systematically and summarised. The structure and physicochemical properties of thiols and their methods of preparation are described and their use as synthons in the preparation of various sulfur-containing compounds is discussed. The bibliography comprises 419 references.

I. Introduction

Thiols play a very important part in living organisms and they are also used in many areas of science and technology. Glutathione and cysteine are known[1] to form part of proteins that are involved in biochemical reactions that take place by an oxidation-reduction scheme, and to bind free radicals. Dihydrolipoic acid takes part in the processes of photosynthesis[2] and metabolism in mitochondria[3] and also in other biochemical reactions.[4] A number of thiols have found applications as pharmaceutical preparations,[5] accelerants of the vulcanisation of rubber,[6,7] polymer stabilisers,[8] and additives to rocket fuels.[9,10] However the most important field of application of thiols is fine-organic synthesis. The lability of S–H and C–S bonds, their ability to undergo fission under the action of both nucleophilic and electrophilic reagents, and the presence of an active reaction centre with sulfur of variable valence all make thiols valuable synthons that are widely applicable in fine-organic synthesis.

The interest being shown in thiols by many investigators has in due course resulted in the appearance of a number of reviews,[4,11–19] which to some or other extent reflect particular aspects of the chemistry of thiols; however many experimental data have been accumulated since the publication of these reviews and these data need futher summarising.

II. The structure and physicochemical properties of thiols

The S–H and C–S bonds in thiols have fairly high dissociation energies but these bonds are not so strong as the O–H and C–O in the oxygen analogues of thiols, i.e. alcohols.

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The structure of the alkyl groups bonded to the sulfur atom in the alkanethiols has almost no effect on the strength of the S–H and C–S bonds; the strength of these bonds is greatly influenced by conjugation of the *p* electrons of the sulfur atom with the π electrons of the system (*p*,π-conjugation).[20,21]

As the electronegativity of the sulfur atom (2.6) is lower than that of the oxygen atom (3.5) thiols have a considerably smaller tendency than alcohols to form hydrogen bonds, as is confirmed by the IR and ^{1}H NMR spectroscopy.[22] This lower tendency to hydrogen-bond formation is responsible for the greater volatility of thiols as compared to alcohols (the boiling points of alkane thiols are 40–60 °C lower than the boiling points of the corresponding alcohols) and also the lower solubility of thiols in water. Thiols are stronger acids than alcohols,[23–27] the S–H bond being more polar than the O–H bond owing to the increased *s* character of the central atom.

Aromatic thiols have a higher acidity than aliphatic thiols owing to the increased polarity of the S–H bond due to *p*,π-conjugation.

The complexes of thiols with shift-reagents[28,29] are less stable than in the case of alcohols, as is shown by the much smaller values of the induced shifts of the resonance signals of the protons in the SH groups as compared to the corresponding values for the protons in OH groups.

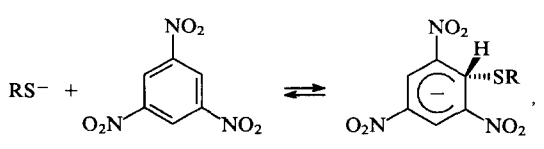
Thiols have a smaller proton affinity than alcohols. The rate of transfer of a proton to thiols in their reaction with trifluoromethanesulfonic acid is several orders of magnitude (10^4–10^5) smaller than the rate of the same reaction for alcohols,[30] as is consistent with the hard-soft-acid-base principle.[31]

$$RSH + CF_3SO_3H \rightleftharpoons \overset{+}{R}SH_2 + CF_3SO_3^-$$

Thiolate anions are weaker bases than alkoxide anions. If the basicity of thiolate anions is judged on the basis of the protonic scale of acidity, using the equilibria

$$RS^- + H^+ \rightleftharpoons RSH; \qquad RO^- + H^+ \rightleftharpoons ROH,$$

the following order of basicities is obtained: $MeO^- > EtS^- > PhO^- > PhS^-$.[4] However, with respect to CH-acids, on the basis of the equilibrium



the order obtained is: $EtS^- > MeO^- > PhS^- > PhO^-$.[32,33]

With respect to CH-acids the thiophenolate anion is a weaker base than the hydroxide anion by a factor of 10^3; this is due to the smaller degree of solvation of thiolate anions as compared to the hydroxide ion.[34] However, thiolate anions are more nucleophilic than either alkoxide anions or the hydroxide anion.

The greater the nucleophilicity of the less basic thiolate anion as compared to the corresponding alkoxide anion may be attributed to the greater polarisability of the sulfur atom as compared to the oxygen atom and also to the transition state in reactions involving a thiolate anion (in the stabilisation of which the *d* orbitals of the sulfur atom are involved) being energetically more favourable. However, one cannot discount the fact that in a protonic solvent oxygen will form a stable hydrogen bond, with the result that it becomes less nucleophilic.

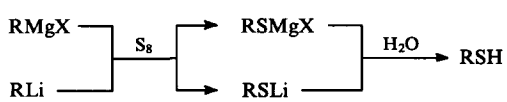
Photolysis, radiolysis, and thermolysis of thiols, and also the action of peroxides and diazo-compounds on them, lead to the production of thiyl radicals.[19] The nature and structure of the groups on the sulfur atom of the thiol have a considerable effect on the enthalpy of formation of the thiyl radicals. For example, arylthiyl radicals have higher enthalpies of formation than alkylthiyl radicals; for the phenylthiyl radical the value is 56.8 ± 2.0 kcal mol^{-1}.[35] The enthalpy of formation of alkylthiyl radicals decreases as the alkyl chain becomes longer and more branched: from 31 kcal mol^{-1} for the methylthiyl radical to 15 kcal mol^{-1} for the butylthiyl and 11 kcal mol^{-1} for the *tert*-butylthiyl radicals.[19] Thiyl radicals have higher electron affinities than oxyl radicals owing to the presence of vacant *d* orbitals on the sulfur atom. Their energy of stabilisation is significantly lower than that of oxyl radicals. For example, Macki[35] quoted 9.6 and 17.5 kcal mol^{-1} respectively for the energies of stabilisation of the phenylthiyl and phenoxyl radicals. The MNDO method has been used to calculate the molecular and electronic structures of the MeS$^{\bullet}$ and EtS$^{\bullet}$ radicals, which have C_s symmetry.[36]

S–H stretches occur in the IR spectra in the 2560 to 2592 cm^{-1} region for alkanethiols and in the 2538–2568 cm^{-1} region for thiols of the aromatic series.[37,38] In the NMR spectra of thiols the signal from the proton of the mercapto-group occurs as a singlet at 1.5–3.5 p.p.m. (δ scale).[39,40] In cyclohexanethiols the mercapto-group occupies an equatorial position preferentially.[41,42] For methanethiol and its carbanion the effective charges on the atoms and the bond orders have been calculated by the CNDO/2 method.[43,44]

III. Methods for preparing thiols

1. Syntheses using elemental sulfur and its inorganic derivatives

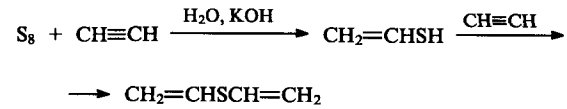
Reactions of elemental sulfur with aromatic hydrocarbons[12,45,46] and some heterocyclic compounds[47] have not been widely used in the synthesis of thiols. This is primarily due to the especially specific conditions for these reactions which are not always reasonable in practice in the laboratory. The reaction of elemental sulfur with organomagnesium and organolithium compounds[4,48,49] proved to be more promising in a preparative respect.



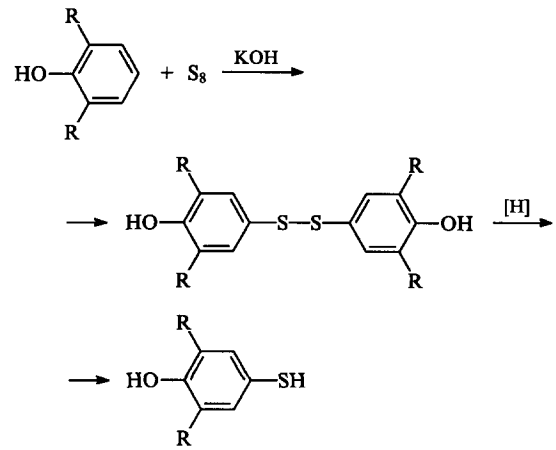
R = Alk, Ar, Het.

The relatively mild conditions for this reaction, and also the availability of the organomagnesium and organolithium compounds, enable a wide range of different thiols to be obtained.

In the reaction of elemental sulfur with acetylene, vinyl thiol is formed[50] and is then converted to divinyl sulfide.

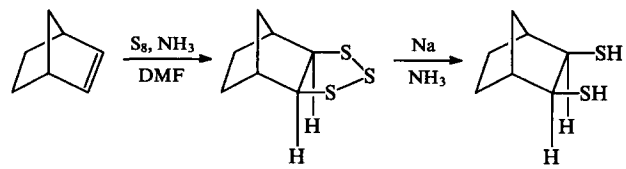


Some reactions of elemental sulfur with organic compounds lead to the formation of disulfides and polysulfides which are readily reduced to the corresponding thiols, e.g. the reaction with dialkylphenols.[51,52]

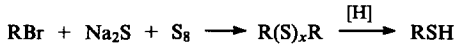


R = Me, Et, Bu^t.

The addition of elemental sulfur to the double bond in norbornene[53] gives the corresponding trisulfide which can be reduced to the dithiol using sodium metal in liquid ammonia.



When mixed with sodium sulfide elemental sulfur also reacts with alkyl halides and highly reactive aryl halides to form polysulfides,[54] the reduction of which gives thiols.



R = Alk, Ar, Het; x = 2–4.

Because of the availability of a wide range of different halide derivatives and also the ease of reduction of the polysulfides, this method is fairly promising in a preparative respect.

Of the inorganic sulfur derivatives the most widely used in the preparation of thiols is hydrogen sulfide. Several variants of thiol preparations based on hydrogen sulfide have been developed. One of these is based on substitution reactions in which halogens, hydroxyl, arenesulfonyl, and other good leaving groups are replaced by a mercapto-group.[55–60]

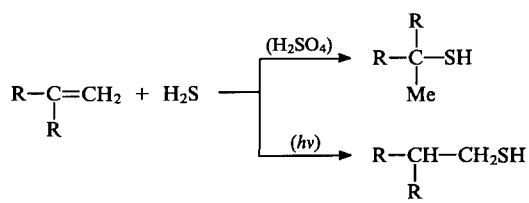


R = Alk, Ar, Het; X = Cl, Br, OTs, OH, NR_2.

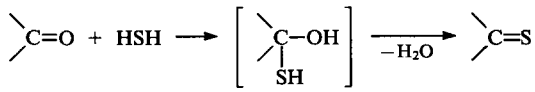
Replacement of a low-activity halogen atom by a mercapto-group in benzene[61-68] and thiophen[69] rings, and also in the vinyl chloride molecule,[70-72] will occur in the vapour phase under relatively severe conditions (400–700°C). In addition to the thiols, the corresponding sulfides and other products are formed, so hindering the isolation of the thiols. These methods therefore have no preparative importance.

The replacement of halogens by a mercapto-group can also be achieved by the action of alkali metal hydrosulfides[73-76] and other inorganic sulfur compounds[77-79] on the corresponding halogen derivatives. As a rule these reactions occur under relatively mild conditions and the wide range and availability of the initial reagents make these methods very valuable in a preparative respect. P_4S_{10} is sometimes used to replace a hydroxyl group by a mercapto-group (see Ref. 80).

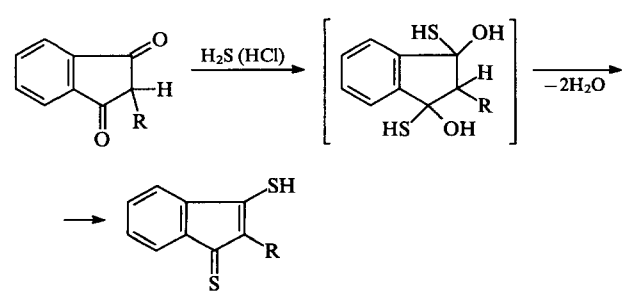
A second variant of thiol preparations based on hydrogen sulfide involves the addition of the latter to unsaturated C≡C, C=C, and C=O bonds. Using irradiation with X-rays, addition of hydrogen sulfide to substituted acetylenes takes place to form dithiols together with other products.[58] The addition of hydrogen sulfide to unsymmetrical ethylene hydrocarbons in the presence of catalysts (H_2SO_4, $AlCl_3$ etc.) takes place preferentially in accordance with Markovnikov's rule but under the action of UV-radiation or in the presence of peroxides the addition is anti-Markovnikov.[55,81-83]



Addition of hydrogen sulfide to the carbonyl group in aldehydes and ketones leads to the formation of 1-hydroxythiols[4] which are stable only if there are strong electron-acceptor groups on the carbonyl carbon atom.

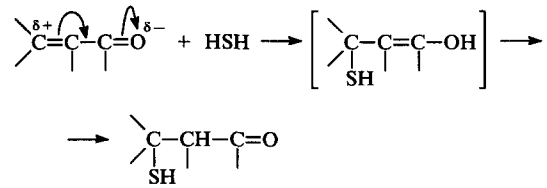


When the molecule of the carbonyl compound contains a labile α-H-atom that can participate in the dehydration process the addition of hydrogen sulfide to the carbonyl group can occur with preservation of a mercapto-group. An example is the preparation of 3-mercaptoindene-1-thiones which are formed in an 85%–90% yield by treating the corresponding diketones with hydrogen sulfide in the presence of hydrogen chloride.[84,85]

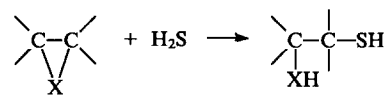


R = H, Et, Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4.

In the presence of catalysts ($ZnCl_2$, HCl etc.) addition of hydrogen sulfide to α,β-unsaturated ketones takes place readily to form relatively stable 3-oxoalkanethiols.[86]



A third variant of the use of hydrogen sulfide in the preparation of thiols involves the opening of unstable rings in certain heterocyclic compounds by the action of hydrogen sulfide. Three-membered heterocyclic compounds, such as thiairans,[87] oxirans,[88] and aziridines[89-91] are used most frequently.



X = S, O, NH.

This method is very important for the preparation of multifunctional thiols containing such groups as NH_2, OH, SH, etc. in addition to the mercapto-group.

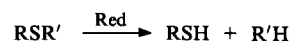
2. Alkylation (or arylation) of sulfur(II) compounds with subsequent breakdown of the products

This method of preparing thiols, which is widely used in practice in the laboratory, is based on forming a C–S bond and then converting the products to thiols. Formation of a C–S bond by means of nucleophilic substitution of a halogen can occur in the reaction of the corresponding alkyl and aryl halides with derivatives of thiocarbonic acid, thiourea, thiocarbamates, dithiocarbamates, xanthogenates, thiophosphonates, and thiosulfonates.[4,77,92,93] These methods are valuable in that the intermediate compounds are readily hydrolysed to thiols; this is very advantageous in a preparative respect and the method is often used in the laboratory to obtain very diverse thiols.

Alcohols in the presence of HBr and dialkyl sulfates are also used for the alkylation of thiourea.[77] Arylation of thiourea and xanthogenates can also be accomplished using diazonium salts.[77]

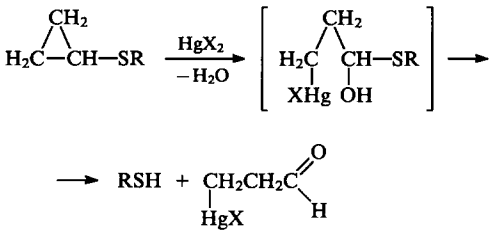
3. Cleavage of sulfides

Although cleavage of a C–S bond occurs more readily than that of a C–C bond or an unactivated C–H bond, the reductive cleavage of sulfides has not been widely used in the preparation of thiols with the exception of special cases. In these cases, as a rule, use is made of sulfides in which there is a distinct tendency to the preferential cleavage of only one of the two C–S bonds, i.e. unsymmetrical sulfides with groups such as allyl, benzyl, nitrile etc. on the sulfur atom.[4]



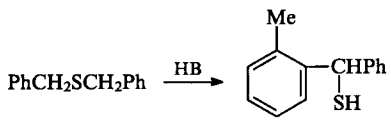
R′ = $ArCH_2$, CH_2=CH–CH_2, CN.

Reducing agents that have been used are lithium in ethylamine, sodium in liquid ammonia, Raney nickel in boiling ethanol, $NaBH_4$ in isopropanol, and also $LiAlH_4$.[94] Cleavage of cyclopropyl-alkyl or -aryl sulfides will take place in the presence of mercury halides or mercury acetate.[95]

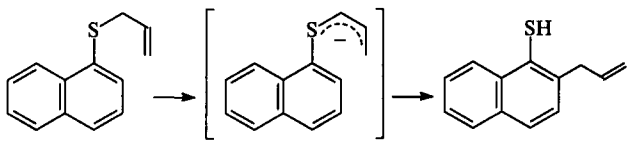


R = Alk, Ar; X = Cl, MeCOO.

Cleavage of alkyl trichloromethyl sulfides[96] is carried out in the presence of hydrochloric acid and that of trifluoromethyl silyl sulfides[97] in the presence of hydrogen iodide. In certain instances reductive cleavage is accompanied by various rearrangements. For example, the cleavage of dibenzyl sulfide in the presence of bases is accompanied by a Sommelet rearrangement.[98]

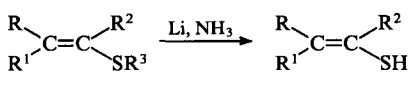


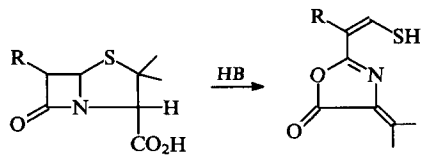
The cleavage of allyl naphthyl sulfides is accompanied by a (3,3)-sigmatropic rearrangement.[99]

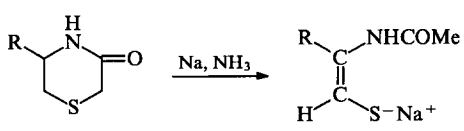


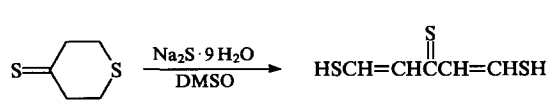
The cleavage of vinyl sulfides by lithium in liquid ammonia[100] provides a method for preparing enethiols, which are also formed by the cleavage of certain heterocyclic compounds.[101-106]

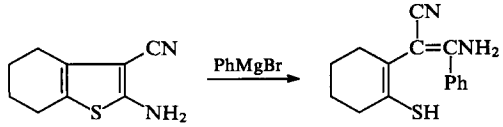
Other heterocyclic compounds, such as penicillin,[107] cyclic allyl sulfides,[108] and thiophene-2-carboxylic acids,[109] will also undergo reductive cleavage to form the corresponding thiols.

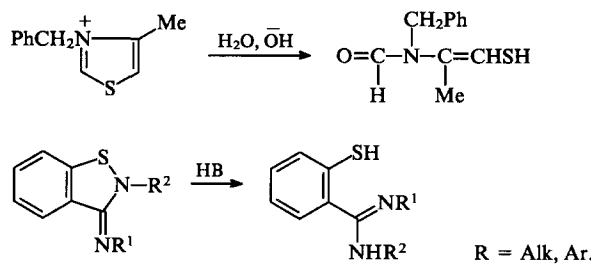








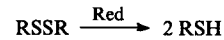




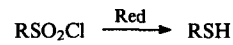
R = Alk, Ar.

4. Reduction of S-functions

The reduction of disulfides and sulfonyl chlorides is of primary importance in the preparation of thiols. The reduction of disulfides is used to prepare aliphatic, aromatic and heterocyclic thiols.



Reducing agents that have been used are zinc in acetic,[110] hydrochloric[111,112] and sulfuric[113] acids, sodium metal in xylene,[114] diethyl ether[115] and liquid ammonia,[116,117] lithium tetrahydroaluminate in ether or tetrahydrofuran,[118] sodium hydrosulfide in alcohol,[119,120] and formamidinesulfinic acid.[121] Triphenylphosphine and sodium hydroborate are also used for the reduction of some disulfides and polysulfides to thiols, and salicylic acid type reagents for the reduction of the disulfide grouping in proteins.[4]



The addition of sulfur monochloride to alkenes followed by reduction of the di-(2-chloroalkyl)disulfides is one of the methods of preparing 2-chloroalkanethiols.[121]

The reduction of sulfonyl chlorides is most often used to prepare aromatic[4,77] and heterocyclic[122] thiols but considerably less often for the preparation of aliphatic thiols.[77]

The reducing agents used are zinc dust in hydrochloric and sulfuric acids,[123-126] tin in hydrochloric acid,[127] tin dichloride,[128] iron powder,[129] aluminium amalgam,[130,131] alkali metal sulfides,[132] red phosphorus and iodine in acetic acid,[133] and lithium tetrahydroaluminate.[134] The last is sometimes used to reduce sulfonic acid to thiols.[135] In rare instances thiols have been prepared by the reduction of sulfinic acids with zinc in an acidic medium[136-138] and of dithiocarbamates with the complex $BH_3 \cdot SMe_2$ in toluene,[139] and also by the reductive cleavage of thiol sulfonates with zinc in an acidic medium.[4]

5. Preparation of thiols from thiones

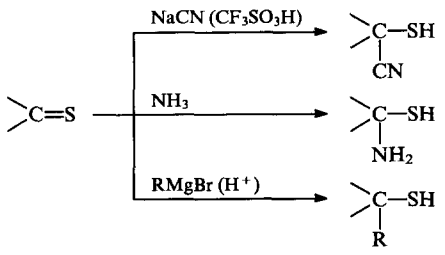
Several variants of thiol preparations based on thiones have been developed. One of these involves the conversion of the thiocarbonyl group to a mercapto-group by the reaction of thiones with butyllithium and also other organometallic compounds.[4,140]



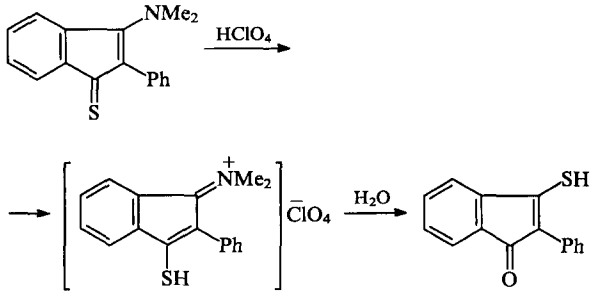
The reaction mixture contains other products as well as thiols, especially sulfides which are formed by the addition of the organometallic compounds at the C = S bond.

It is presumed[4] that the intermediate products in this reaction are dianions formed by the reaction of the thiones with the organometallic compounds. This hypothesis is confirmed to some extent by the fact that the dianion of thiobenzaldehyde is converted to the corresponding thiols and sulfides by reaction with electrophilic reagents.[141]

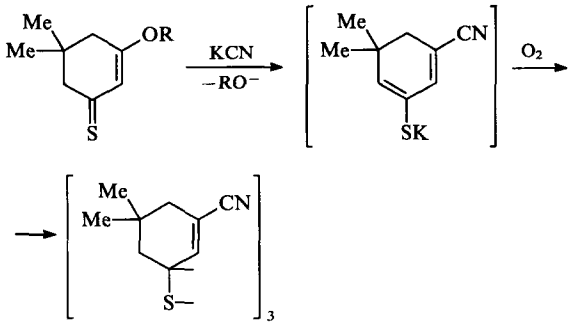
The corresponding thiols are also formed by the reaction of a thiocarbonyl group with hydrocyanic acid,[142,143] ammonia,[144] or Grignard reagents.[145]



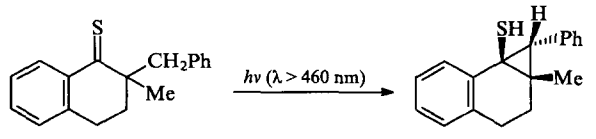
Participation of the thiocarbonyl group in a conjugated bond system facilitates its conversion to a mercapto-group. For example, 3-(*N*,*N*-dimethylamino)-2-phenylindene-1-thione is readily converted, in the presence of perchloric acid in acetone, to *N*,*N*-dimethyl-3-mercapto-2-phenylinden-1-iminium perchlorate which undergoes hydrolysis at the C=N bond to form 3-mercapto-2-phenylinden-1-one.[146]



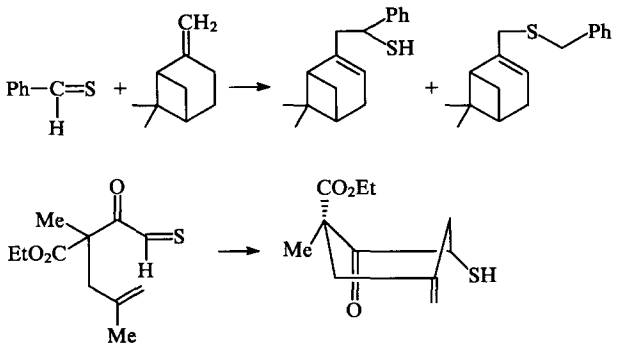
3-Alkoxy-5,5-dimethylcyclohex-2-ene-1-thiones are readily converted, by reaction with potassium cyanide in methanol, to potassium 3-cyano-5,5-dimethylcyclohexa-2,6-diene-1-thiolate, which trimerises to a 1,3,5-trithiane.[147]



2-Benzyl-2-methyltetralin-1-thione is readily converted to an isomeric thiol by UV-irradiation.[148]

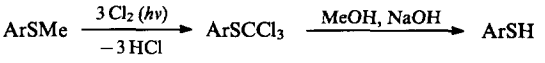


A thiocarbonyl group as a 2π-component can participate in an addition reaction to a C=C bond to form thiols.[149,150]

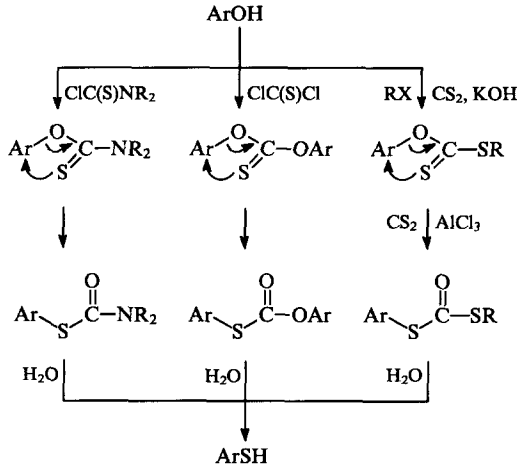


6. Other methods for preparing thiols

One of the methods for converting methyl aryl sulfides to thiophenols is exhaustive chlorination of the methyl group followed by methanolysis of the chlorination product.[151]



The Newman–Kwart rearrangement forms the basis of a method for converting phenols to thiophenols.[4]



The condensation of thiourea with various bifunctional compounds and also the reaction of carbon disulfide with amino- and hydroxyl-containing compounds are widely used in the preparation of heterocyclic thiols.[4,77,152–154]

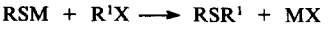
IV. Preparations based on thiols

1. Preparation of sulfur(II) compounds

a. Preparation of sulfides

Several methods have been developed for preparing sulfides from thiols.

Alkylation or arylation of thiols. Symmetrical and unsymmetrical sulfides are formed relatively easily by the reaction of thiols[77,155–159] and metal thiolates[160–171] with alkyl and aryl halides.

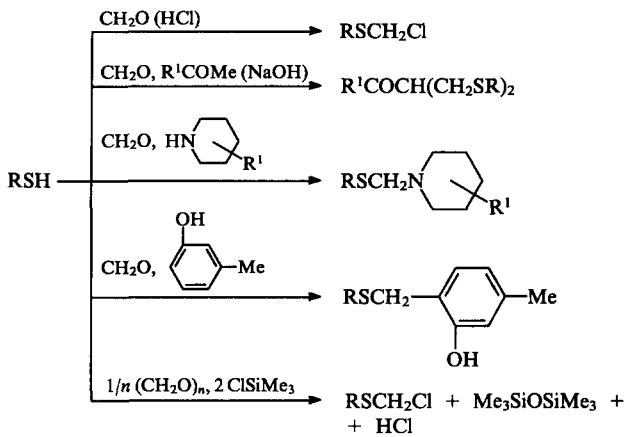


M = H, Na, K, Ag; X = Cl, Br, I;
R = Alk, Ar, Het; R^1 = Alk, Ar.

It is preferable to use alkyl bromides in these reactions because alkyl chlorides are not always sufficiently reactive and alkyl iodides may cause side reactions in which disulfides are formed.[4,77]

$$2RSH + R^1I \longrightarrow RSSR + R^1H + HI$$

The formation of disulfides is also observed when certain alkyl chlorides, especially diphenylchloromethane[172] and carbon tetrachloride,[173] are used. In certain instances the following can be used as alkylating agents: alcohols in the presence of mineral acids,[77,174,175] sodium alkoxides in the presence of phosphonium salts,[176] dialkyl sulfates,[4] dialkyl carbonates,[177,178] alkyl esters of phosphorus acid,[179] phosphoric acid,[180] nitric acid[181] and alkylsulfinic acids,[182] alkoxyformamidines,[183] methyl esters of phenols,[184] alkylamines[185] and diamines,[186] epoxy-[187,188] and thioepoxy-compounds,[4] ethyleneimines,[77] and pyridinium,[189] sulfonium,[190] iodonium[191] and diazonium[77] salts. For the preparation of sulfides containing a methylene group formaldehyde,[192-195] paraformaldehyde[196,197] and trioxane[198] are widely used in a variety of reactions.



The alkylation of thiols by alkyl halides with a normal structure usually takes place by an S_N2 mechanism in which the transition state is additionally stabilised by *d*-orbital resonance.[4]

The reaction of triphenylchloromethane with thiophenol in the presence of bronze filings takes place by a radical mechanism.[199]

$$Ph_3CCl \xrightarrow{\text{bronze}} Ph_3C^{\cdot} + Cl^{\cdot}$$

$$Ph_3C^{\cdot} + PhSH \longrightarrow Ph_3CH + PhS^{\cdot}$$

$$PhS^{\cdot} + Ph_3C^{\cdot} \longrightarrow PhSCPh_3$$

The reactions of perfluoroiodomethanes[200-208] and perfluorobromomethanes[209] with thiolates take place in ultraviolet light by an ion-radical mechanism $S_{RN}1$ (see Ref. 210).

$$RS^- + CF_3I \longrightarrow RS^{\cdot} + [CF_3I]^{\cdot -}$$

$$[CF_3I]^{\cdot -} \longrightarrow \dot{C}F_3 + I^-$$

$$RS^- + \dot{C}F_3 \longrightarrow [RS^{\cdot} + \bar{C}F_3] \longrightarrow [RSCF_3]^{\cdot -}$$

$$[RSCF_3]^{\cdot -} + CF_3I \longrightarrow RSCF_3 + [CF_3I]^{\cdot -}$$

It has been shown[211,212] that the ion-radical perfluoroalkylation reaction is of a general character and can be used with perfluoroalkyl iodides and bromides of any chain length and structure, and also with α,ω-di-iodoperfluoroalkanes.

The reaction of CF_2Br_2 with thiophenoxides takes place by a chain-type carbene mechanism.[213]

$$RS^- + BrCF_2Br \longrightarrow \bar{C}F_2Br + RSBr$$

$$\bar{C}F_2Br \longrightarrow :CF_2 + Br^-$$

$$:CF_2 + RS^- \longrightarrow RS\bar{C}F_2$$

$$RS\bar{C}F_2 + BrCF_2Br \longrightarrow RSCF_2Br + \bar{C}F_2Br$$

It has been shown[206,213] that in the reaction of CF_2BrCl and $PhSCF_2Br$ with thiolates two mechanisms, a carbene and an ion-radical mechanism, may coexist whereas the reaction of $ClCH_2CF_2Cl$, $BrCH_2CF_2Cl$, and $CHCl_2CF_2Cl$ with thiolates takes place via a stage in which hydrogen chloride is eliminated and addition of the thiolate anion to the difluoromethylene group of the halogeno-olefin occurs.[214] One cannot exclude the possibility that replacement of a halogen atom on an unsaturated carbon atom also takes place via a stage in which the hydrogen halide is eliminated.[215-218]

Thus the alkylation of thiols by alkyl halides may take place by different mechanisms, depending primarily on the structure of the initial alkyl halide and also the conditions under which the alkylation reaction is carried out; this has been discussed in detail in a monograph.[219]

The arylation of thiols (or thiolates) by aryl halides in which the halogen atom is activated by the presence of strong electron-acceptor groups in the *ortho* and *para* positions take place relatively easily by an S_N2ar mechanism, the *d* orbitals of the sulfur atom being involved in the stabilisation of the σ-complex.[4,77,220-222] Not only halogen atoms but also other atoms or groups (NO_2, H etc.) which are activated by strong electron-acceptor *ortho* and *para*-substituents can be replaced by an RS group.[34,223] Replacement of an unactivated halogen atom in an aromatic ring by an RS group will take place under relatively severe conditions,[224-232] presumably by an elimination-addition mechanism.[227] Arylation of the silver salt of trifluoromethanethiol can be accomplished using aryldiazonium salts.[228]

Thiylation of unsaturated compounds. Sulfides are formed relatively easily by the addition of thiols to unsaturated bonds (C=C, C=O, and C=N). The addition of thiols to compounds containing a C=C bond has been known for a long time and has been comparatively well studied.[4,11,12] Many of these reactions form the basis of methods for preparing sulfides.

Depending on the conditions, the addition of thiols to an ethylenic bond may occur by a nucleophilic, an electrophilic, or a radical mechanism. Nucleophilic addition of a thiol to an ethylenic bond usually takes place in an alkaline medium or in the presence of basic catalysts and the species attacking the sp^2-hybridised carbon atom are thiolate anions.

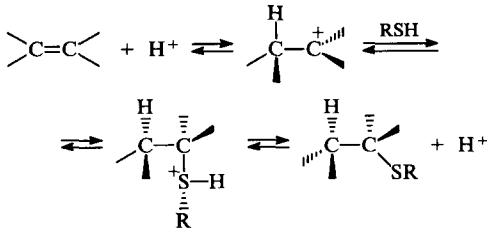
$$RSH + \bar{O}H \longrightarrow RS^- + HOH$$

$$RS^- + \rangle C{=}C\langle \longrightarrow RS{-}\overset{|}{C}{-}\overset{|}{\bar{C}}{-} \xrightarrow{HOH} RS{-}\overset{|}{C}{-}\overset{|}{C}H{-}$$

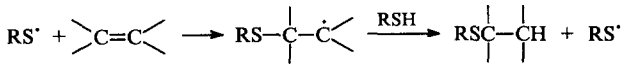
Nucleophilic addition of thiols to a polarised double bond will therefore take place readily if there are electronegative atoms or electron-acceptor groups present at the double bond. The thiyl fragment is attached to the electron-deficient carbon atom in the double bond which is usually in the β position (addition in accordance with Markovnikov's rule). There have been reports of the nucleophilic addition of thiols to acrolein,[77] vinylidene chloride[229,230] acrylonitrile,[231,232]

unsaturated carboxylic acids and their esters,[232-235] also other unsaturated carbonyl compounds,[235-239] unsaturated sulfones,[240,241] vinylpyridines,[242] vinylpyrroles,[243] and vinylpyrazoles.[244] The nucleophilic addition of thiols to maleinimides is used for the modification of thiol enzymes in studies of the interrelation of their structure and function.[4] For example, to determine the number of SH groups in proteins, and also to ascertain the reactivity of these groups, use is often made of the fluorescing agent *N*-(fluoranthen-3-yl)maleinimide, which combines with the protein by reacting with its SH groups.

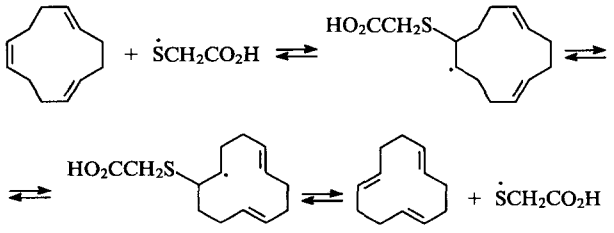
Electrophilic addition of thiols to a double bond[244,245] takes place in an acidic medium or in the presence of acidic catalysts (HCl, $AlCl_3$, SO_2Cl_2 etc.) via a stage in which a carbocation is formed.[12]



Anti-Markovnikov radical addition of thiols to a double bond takes place in the presence of peroxides or under the influence of ultraviolet light (photo-addition) and is often accompanied by isomerisation of the initial unsaturated compounds.[11,12,246]

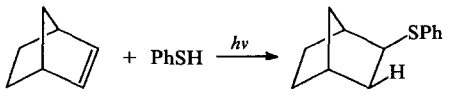


The involvement of thiyl radicals in the isomerisation of unsaturated compounds has been noted.[4] For example, in the presence of 1 equivalent of thioglycolic acid (*Z*, *E*, *E*)-cyclododeca-1,5,9-triene is readily converted to the corresponding (*E*, *E*, *E*)-isomer by an 'insertion–detachment' mechanism.[247]

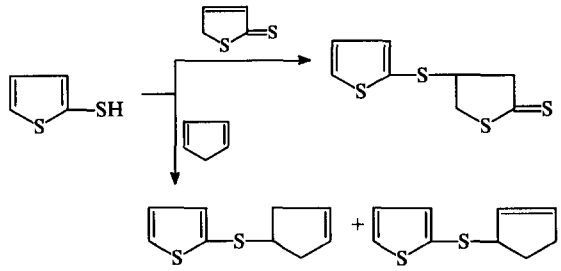


On account of the unusual tendency of thiyl radicals to react preferentially with the (*Z*)-alkene grouping, this method of isomerisation has been used in organic syntheses, especially for the conversion of oleic acid to (*E*)-octadec-9-enoic acid which will take place in the presence of ethanethiol.[248]

The photo-addition of thiols to a C=C bond usually gives products whose stereochemistry is dependent on the structure of the initial unsaturated compound. For example, in the photothiylation of norbornene an *exo-cis* adduct is formed.[4]



In view of the fact that thiyl radicals are easily obtained from thiols, e.g. by irradiation with light of wavelength 253.7 nm, it is likely that the autothiylation of thiophen-2-thiol[249,250] and the addition of the latter to cyclopentadiene[251] also take place by a radical addition mechanism.

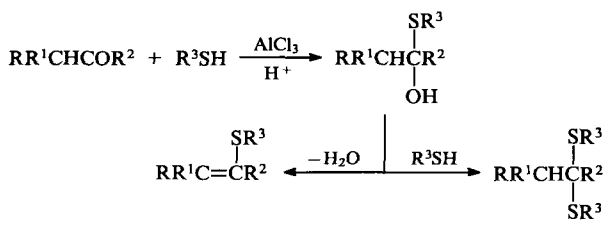


Unsaturated sulfides are also readily formed by the addition of thiols to acetylenic hydrocarbons.[4,11,12] The addition of thiols to a triple bond may take place by either a nucleophilic or a radical mechanism. Nucleophilic addition of thiols to an acetylenic bond takes place in an alkaline medium and, depending on the reaction conditions, the type of solvent, and also the structure of the reagents, it can give products with different steric structures. There have been reports of the nucleophilic addition of thiols to acetylene,[252,253] phenylacetylene,[254,255] alkoxyacetylenes,[256-258] acetylacetylenes,[259,269] acetylenecarboxylic acids and their derivatives,[261-263] diethoxyphosphonylacetylene,[264] alkylsulfonylacetylenes,[265] trialkylgermylacetylenes,[266] and diacetylenes.[267] The nucleophilic addition of thiols to alkylthioacetylenes,[12,268] occurs particularly easily due to the additional stabilisation of the intermediate carbanion involving the 3*d* orbitals on the sulfur atom.



Radical addition of thiols to a triple bond takes place on irradiation with ultraviolet light or in the presence of initiators of radical processes (peroxides, hydroperoxides, azo-compounds etc.) that facilitate the generation of thiyl radicals. The radical addition of thiols to acetylene[269,270] will occur under severe conditions but the addition of thiols to prop-2-yn-1-ol,[12] phenylacetylene,[12] ethoxyacetylene,[271] ethoxycarbonylacetylene,[271] acetylenecarboxylic acid,[271] 1-carboxy-2-ethylthioacetylene,[272] vinylacetylene,[273] trialkylsilylacetylene,[274,275] and 1-phenyl-2-trialkylsilylacetylene[276] takes place comparatively easily by a radical mechanism.

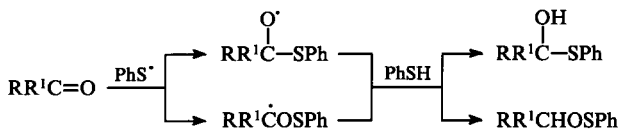
The addition of thiols to the C=O bond in carbonyl compounds in the presence of acidic catalysts produces unstable sulfides containing an α-hydroxyl group which can undergo dehydration to form unsaturated sulfides[277] or react with excess of the thiol to give thioacetals.[278,279] This method of obtaining thioacetals has been widely used in the laboratory for preparative purposes.



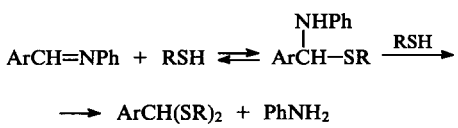
The addition of thiols to carbonyl compounds in the presence of trialkylchlorosilanes results in the formation of sulfides containing a trialkylsiloxy group in the α-position.[280]



In the radical addition of thiols to the C=O bond in carbonyl compounds the thiyl radical may be attached to either the carbon or the oxygen atom of the carbonyl group.[281,282]



The addition of thiols to the C=N bond in imines results in the formation of α-aminosulfides which, in the presence of excess of the thiol, can also be converted to thioacetals;[283-287] this method is of preparative importance and is widely used in the laboratory.



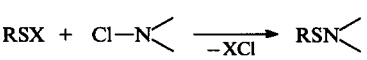
Condensation of thiols. The intermolecular condensation of thiols, which occurs at high temperatures or in the presence of catalysts, is sometimes used to obtain sulfides.



In the case of β-mercaptoanthraquinone condensation takes place with little heating[77] but with other aromatic thiols it occurs at higher temperatures.[224] By using such catalysts as cadmium or zinc sulfide, aluminium oxide[77] or aluminium trichloride[286,287] the temperature of this reaction can be reduced slightly.

b. Preparation of sulfenamides.

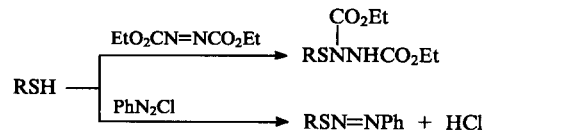
The amination of thiols by *N*-chloroamines,[288-290] *N*-chloroamides,[291] or *N*-chloroimides[292-294] is one of the methods of preparing sulfenamides that are either unsubstituted or substituted at the nitrogen atom.

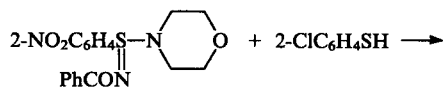


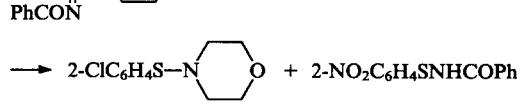
R = Alk, Ar, Het;

X = Na, H.

Rather more rarely aliphatic amines in the presence of oxidising agents,[290,295] the sodium salt of hydroxylaminosulfonic acid,[296] and derivatives of oxaziridine[297] have been used as aminating agents. Sulfenamides are also formed by the reaction of thiols with azo- and diazo-compounds[4] and with certain derivatives of iminosulfinic acids[298] but these methods have no preparative value.

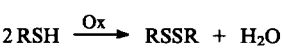




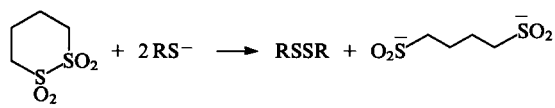


c. Preparation of disulfides

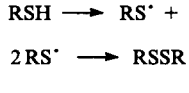
The oxidation of thiols using various oxidising agents is one of the most common methods of preparing disulfides.[4]



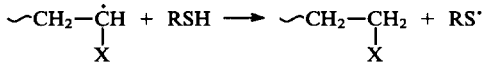
A wide range of reagents can be used as oxidants, including oxygen,[299] hydrogen peroxide,[300] halogens and halogenating agents,[4,301-304] *N*-halogenoamines and *N*-halogenoamides,[4,305] iron trichloride,[77] 1,3-di-iodopropyne,[306] carbon tetrachloride,[307] and other organic and inorganic reagents. On account of the possible further oxidation of the disulfides the choice of a suitable oxidant is of considerable importance and is conditional on the ease of oxidation, which increases from tertiary to secondary and primary mercaptans and even more for thiophenols.[77] The oxidation of a mercapto-group to a disulfide group plays an important role in the formation of the tertiary structure of proteins and also in other biochemical processes. Flavins will anaerobically oxidise an excess of a thiol to a disulfide and are reduced to dihydroflavins.[308] The tetraoxide of 1,2-dithiane oxidises thiolate ions to the disulfide quantitatively.[309]



This reaction is presumed to occur in biological systems.[4] In the presence of pyridine the dimethyl ester of dithiobis(thioformic acid) oxidises thiols to disulfides in a quantitative yield.[310] Photolysis or radiolysis of thiols and sulfides gives thiyl radicals which form disulfides by recombination or reaction with the solvent molecules.[4,311,312]



Owing to the ease with which thiyl radicals are formed, thiols are used as radical interceptors in various processes such as radiation protection,[4] the stabilisation of polymeric materials,[8] and the control of chain growth in radical-chain reactions.[313] For example, dodecyl mercaptan is widely used in industry as a regulator of molecular mass.[314] The basis of this process is the reaction:



A whole series of methods for preparing both symmetrical and unsymmetrical disulfides is based on nucleophilic substitution involving thiols or thiolate anions and various sulfenyl derivatives such as sulfenyl halides,[315-327] sulfenyl thiocyanates,[4,77,328] sulfenamides,[329-333] symmetrical disulfides[334-336] and tri-sulfides,[337] thiosulfonates,[4,77] and Bunte salts.[4,77]

$$RSX + R^1SY \longrightarrow RSSR^1$$

R = Alk, Ar, Het; R^1 = Alk, Ar; X = H, Na, Ag;
Y = Cl, Br, NR^2, NHAr, N-phthalimido,
SR^2, SSR^2, SO_2Ar, SO_2Na, SCN.

In view of the extensive possibilities for varying R and R^1, some of these methods, especially the reaction of thiols with sulfenyl halides, have become irreplaceable for the synthesis of unsymmetrical disulfides.

The esters $RSSCO_2Me$, which are obtained by the reaction of thiols with methoxycarbonylsulfenyl chloride, readily react with thiols to form disulfides.

$$RSH + MeO_2CSCl \longrightarrow RSSCO_2Me \xrightarrow{R^1SH} RSSR^1 + HO\overset{\overset{S}{\|}}{C}OMe$$

The so-called cyanogen bromide method for converting thiols to unsymmetrical disulfides[339] involves the reaction of the thiol with a sulfenyl bromide which is formed by the reaction of cyanogen bromide with a sodium thiolate.

$$RSNa + BrCN \xrightarrow[-NaCN]{} [RSBr] \xrightarrow[-HBr]{R^1SH} RSSR^1$$

A convenient method for obtaining unsymmetrical disulfides is the reaction of thiols with the diethyl ester of azodicarboxylic acid followed by cleavage of the resultant adduct.[4]

$$RSH + EtO_2CN{=}NCO_2Et \longrightarrow EtO_2CNH\overset{\overset{SR}{|}}{N}CO_2Et \xrightarrow{R^1SH} RSSR^1 + (EtO_2CNH)_2$$

d. Preparation of thiocyanates and sulfenyl thiocyanates.
The reaction of thiolate anions or heavy metal thiolates with cyanogen halides leads to the formation of thiocyanates.[4] This reaction has been used as a basis for developing the synthesis of labelled thiocyanates.[340]

$$RSH + BrCN \xrightarrow[-HBr]{} RSCN \xrightarrow{^{35}\bar{S}H} R^{35}SH \xrightarrow{BrCN} R^{35}SCN$$

4-Dimethylamino-1-cyanopyridinium perchlorate and fluoroborate[341] and 2-nitro-5-thiocyanatobenzoic acid[342] have also been used as cyanating agents.

The reaction of thiols with thiocyanogen gives sulfenyl thiocyanates and the further reaction of these products with the thiol can give a disulfide. This sequence of reactions has been proposed as a basis for synthesising cystine.[343]

$$XSH + (SCN)_2 \longrightarrow XSSCN \xrightarrow{HSY} XSSY$$

X = $HO_2C\overset{\overset{NH_2}{|}}{C}HCH_2$; Y = $HO_2C\overset{\overset{NH_2\cdot HCl}{|}}{C}HCH_2$

e. Preparation of thionitriles and thionitrates
Thiols react with nitrous acid in the cold to form *S*-nitroso-compounds or thionitrites; these are comparatively stable only in the case of tertiary thiols.[344]

$$RSH + HONO \xrightarrow{0\,^\circ C} RSNO + H_2O$$

R = Bu^t, MeCO.

Nitrosyl chloride and esters of nitrous acid are also used as nitrosating agents.[344] The reaction of thiols with an equivalent quantity of nitrogen(IV) oxide also results in the formation of thionitrites which, in the presence of excess of the oxide, are converted to thionitrates.[345]

$$RSH \xrightarrow{N_2O_4} RSNO \xrightarrow{N_2O_4} RSNO_2$$

R = Bu^t, MeCO.

f. Preparation of thiolic esters
The acylation of thiols with acyl chlorides is the main method of preparing thiolic esters of carboxylic acids.[77]

$$RSH + R^1COCl \xrightarrow[-HCl]{} RS\overset{\overset{O}{\|}}{C}R^1$$

This reaction often proceeds very smoothly even in the absence of bases but it is usually carried out by the Schotten–Baumann method[77] or in the presence of pyridine and triethylamine. Thiolates of alkali metals[346] and other metals[347] are sometimes used instead of thiols, and carboxylic acids[348,349] and their anhydrides[350] and acyl azides[346] are also used as acylating agents. The addition of thiols to ketene gives thiolic esters of acetic acid[4] but this method is hardly used in the laboratory because ketene is not readily available.

$$RSH + CH_2{=}C{=}O \longrightarrow RSCOMe$$

The preparation of thiolic esters of benzenesulfinic acid by the reaction of thiols with benzenesulfinyl azide has been reported.[351]

$$PhSON_3 + RSH \xrightarrow[-HN_3]{20\,^\circ C} PhS\overset{\overset{O}{\|}}{S}R$$

Thiolic esters of sulfonic acids are formed by the reaction of sodium thiolates with sulfonyl chlorides.[352]

$$RSNa + PhSO_2Cl \xrightarrow[-NaCl]{} PhSO_2SR$$

g. Preparation of compounds containing Si–S bonds
Alkali metal thiolates react with silicon tetrachloride comparatively easily to form tri(alkylthio)chlorosilanes or tetra(alkylthio)silanes, depending on the reagent ratio.[353,354]

$$SiCl_4 \xrightarrow[-3\,NaCl]{3\,RSNa} (RS)_3SiCl$$
$$SiCl_4 \xrightarrow[-4\,NaCl]{4\,RSNa} (RS)_4Si$$

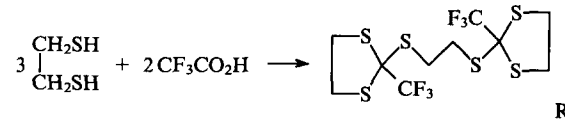
R = Me, Et, Pr.

Trihalogenoalkylsilanes,[355] trialkylchlorosilanes,[356,357] and alkylsilazanes[358,359] can also be used for the silylation of thiols.

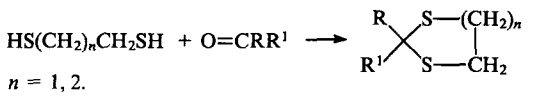
h. Preparation of heterocyclic compounds

A whole series of syntheses of various heterocyclic compounds have been developed on the basis of reactions characteristic of SH groups. These syntheses usually involve the use of thiols containing two SH groups or polyfunctional thiols.

Syntheses based on dithiols

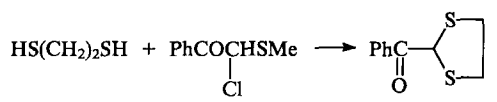


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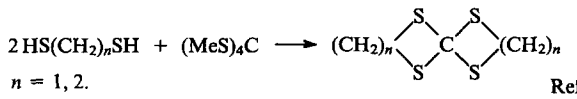


n = 1, 2.

Ref. 361

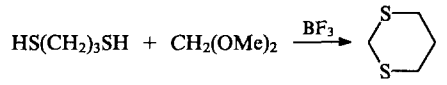


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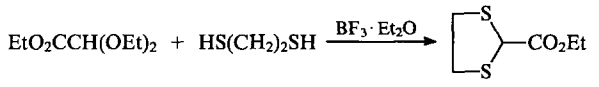


n = 1, 2.

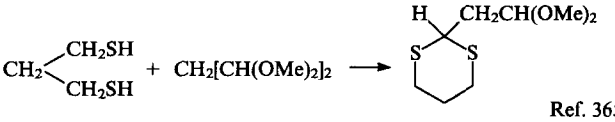
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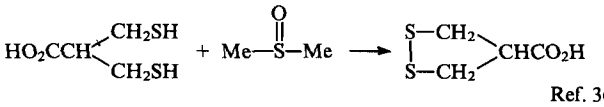
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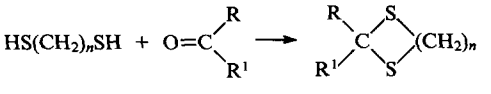
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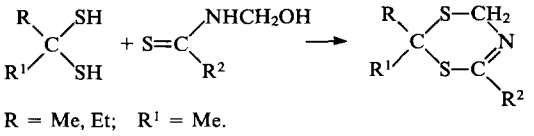


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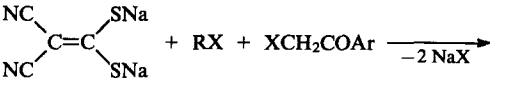
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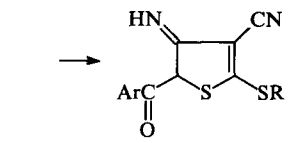
R = Me, Et; R^1 = Me.



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

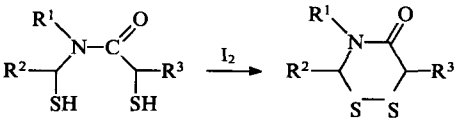
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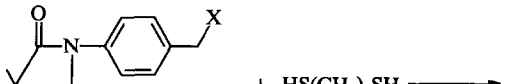
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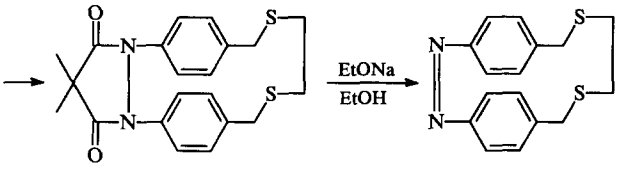
R = Me, Et; Ar = Ph, 4-ClC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$.



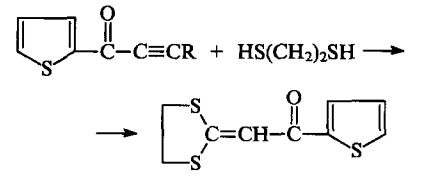
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R^1 = Alk; R^2 = CONHPh, CO_2Et.

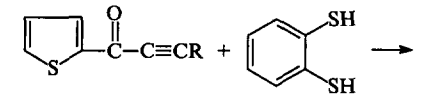




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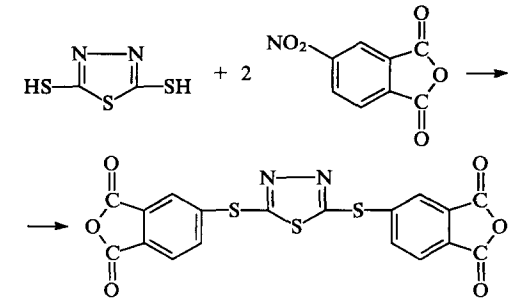


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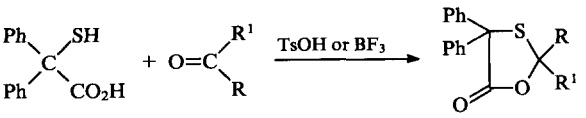
Ref. 371

R = H, Ph.

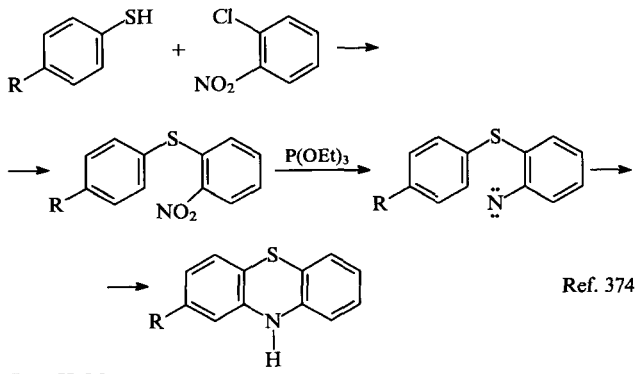


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Syntheses based on polyfunctional thiols

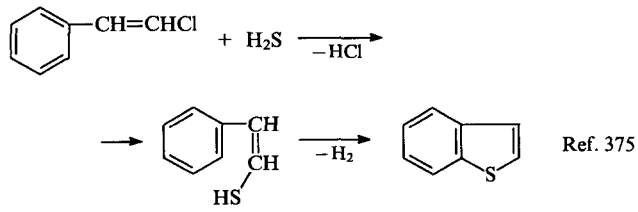


R = Me, Et; R^1 = Me. Ref. 373

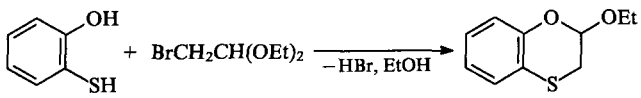


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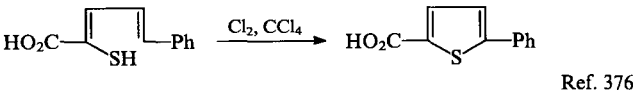
R = H, Me.



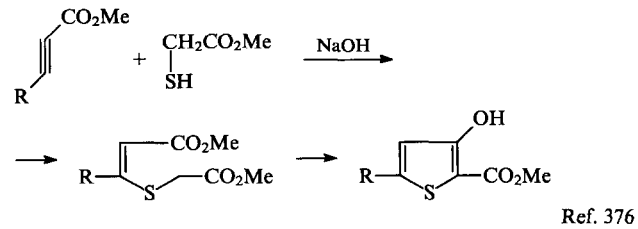
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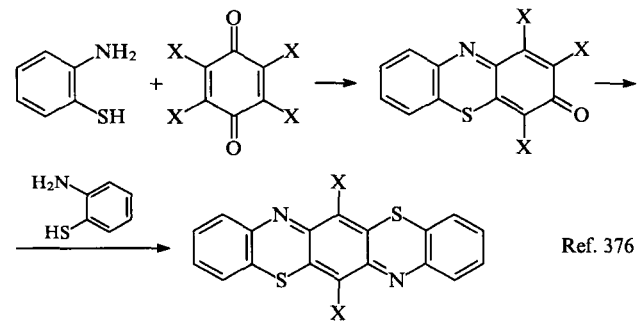


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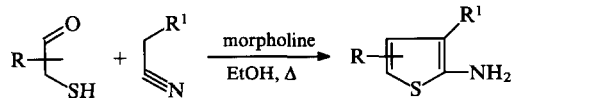
Ref. 376

R = H, Me.



Ref. 376

X = Cl, Br.



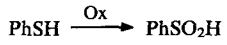
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R = Me, Et; R^1 = H, Me.

2. Preparation of sulfur(IV) compounds

a. Preparation of sulfinic acids and their derivatives

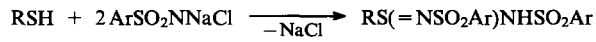
The oxidation of thiols in order to obtain sulfinic acids is only used in rare instances because the sulfinic acids formed can easily be oxidised to sulfonic acids. However in certain instances[4,377-379] oxidation is nevertheless used for the preparation of sulfinic acids.



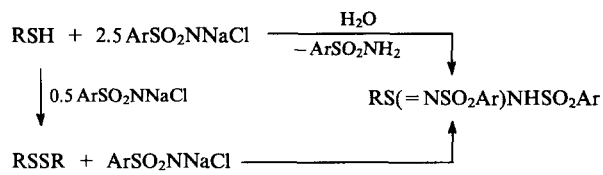
The oxidising agents used are chlorine, bromine, iodine, hydrogen peroxide, and *m*-chloroperbenzoic acid. Oxidative chlorination of thiols is sometimes used to prepare sulfinyl chlorides.[380,381] Esters of sulfinic acids are formed by oxidising thiols with lead tetra-acetate in the presence of alcohols.[4]

b. Preparation of amides of iminosulfinic acids

Oxidative imination of thiols with *N*-chloro-compounds. The first examples of amides of iminosulfinic acids, viz. *N*-(arenesulfonyl)amido-*N'*-(arenesulfonyl)-iminosulfinic acids or *N*,*N'*-bis(arenesulfonyl)sulfinamidines, were obtained by the reaction of thiols with sodium salts of chloroamides or sulfonic acids in aqueous solution.[382]



The yield of the sulfinamidine in this reaction is low because some of the sodium salt of the chloroamide is used to oxidise the thiol to a disulfide.



The formation of disulfides as intermediates has also been observed in the oxidative imination (using sodium salts of the chloroamides of sulfonic acids) of alkanethiols,[383] arylthiols,[384] 8-mercaptoquinoline,[385] and arylcarbamoyl-[386] and alkoxycarbonyl-methanethiols.[387] It follows that the imination of thiols and of disulfides by sodium salts of chloroamides of sulfonic acids are similar processes and the first stage of the imination of a thiol is its oxidation to a disulfide. This stage is not rate-determining because the rate of oxidation of the thiols to disulfides by various oxidising agents decrease in the order ArSH > $ROOCCH_2SH$ > AlkSH,[82] whereas the reactivity of thiols towards the sodium salts of chloroamides of sulfonic acids varies in the reverse order and is dependent on their acidic properties.[384] Thiols with $pK_a > 7$ undergo imination by the sodium salts of chloroamides comparatively readily. A reduction in the pK_a of the thiol to 5–6 leads to a reduction in the rate of imination and in the yield of the sulfinamidine. Thiols with $pK_a < 5$ do not undergo imination by the sodium salts of the chloroamides of sulfonic acids. Such thiols usually have strong electron-acceptor groups on the sulfur atoms, so making it less nucleophilic. Imination of thiols by *N*-chloroamides of carboxylic acids[388,389] and phosphoric acids[390] can be carried out in anhydrous organic solvents in the presence of pyridine.

$$2\,RSH + 5\,AcNHCl + 4\,C_5H_5N \longrightarrow$$
$$\longrightarrow 2\,RS(=NAc)NHAc + AcNH_2 + C_5H_5N\cdot Cl_2 + 3\,C_5H_5N\cdot HCl$$

R = Alk, Ar, Het; Ac = ArCO, $(PhO)_2PO$.

Oxidative imination of sodium thiolates with *N*-dichloro-compounds. The reaction of sodium thiolates with the dichloroamides of sulfonic acids in anhydrous organic solvents gives the sodium salts of *N,N'*-disubstituted amides of iminosulfinic acids.[391]

$$5\,RSNa + 2\,ArSO_2NCl_2 \xrightarrow[-4\,NaCl]{}$$
$$\longrightarrow RS(=NSO_2Ar)N(Na)SO_2Ar + 2\,RSSR$$

This reaction has been widely used for alkanethiols,[383,392] derivatives of thiourea,[393] 8-mercaptoquinoline,[394-397] and other heterocyclic thiols.[398-400] The dichloroamides of carboxylic acids[401-404] and phosphoric acids[405] and also *N,N*-dichlorodicyanoethylurea[406] have been used as iminating agents. The reactivity of the sodium thiolates towards the *N*-dichloroamides is dependent on the acidic properties of the thiol.[407] The sodium salts of thiols with $pK_a > 8$ undergo imination by *N*-dichloroamides comparatively readily but a reduction in the pK_a of the thiol to 5–7 lead to a reduction in the reactivity of the sodium thiolate towards *N*-dichloroamides. The sodium salts of thiols with $pK_a < 5$ do not undergo imination by *N*-dichloroamides. The intermediates in this reaction were found[408] to be *N*-(arylsulfenyl)-*N,N'*-bis(arenesulfonyl)arylsulfinamidines which are also formed in the reaction of sodium thiophenolates with dichloroamides of sulfonic acids in anhydrous carbon tetrachloride when the reagents are in a 4:2 ratio.[409]

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

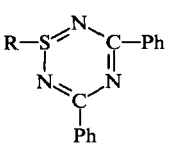
It is presumed[408] that these compounds are formed due to the following reactions:

$$2\,RSNa + 2\,ArSO_2NCl_2 \longrightarrow 2\,RSCl + 2\,ArSO_2NNaCl;$$
$$2\,RSCl + 2\,RSNa \longrightarrow 2\,RSSR + 2\,NaCl;$$
$$2\,ArSO_2NNaCl + RSSR \xrightarrow[-2\,NaCl]{} RS(=NSO_2Ar)N(SR)SO_2Ar.$$

In the presence of an additional mole of the sodium thiophenolate cleavage of the *N*-(arylsulfenyl)-*N,N'*-bis(arenesulfonyl)arylsulfinamidine takes place to form a disulfide and the sodium salt of the *N,N'*-bis(arenesulfonyl)arylsulfinamidine.[408]

$$RS(=NSO_2Ar)N(SR)SO_2Ar + RSNa \longrightarrow$$
$$\longrightarrow RS(=NSO_2Ar)N(Na)SO_2Ar + RSSR$$

The reaction of sodium thiolates with *N*-chloro- and *N*-bromobenzamidines gives cyclic amides of iminosulfinic acids.[410]

$$RSNa + 2\,PhC(=NH)NHX \longrightarrow$$
$$\longrightarrow$$  $$+ NH_4X + NaX$$

X = Cl, Br.

c. Preparation of iminosulfinyl chlorides

The formation of iminosulfinyl chlorides by the reaction of thiophenols with dichloroamides of sulfonic acids may take place via the following reactions, depending on the reagent ratio and the order in which the reagents are mixed[484] [incorrect reference (Ed. of Translation)]:

$$2\,ArSH + PhSO_2NCl_2 \longrightarrow 2\,ArSCl + PhSO_2NH_2;$$
$$2\,ArSCl + 2\,PhSO_2NCl_2 \longrightarrow 2\,ArS(=NSO_2Ph)Cl + Cl_2;$$
$$2\,ArSCl + 2\,ArSH \xrightarrow[-2\,HCl]{} 2\,ArSSAr;$$
$$ArSSAr + 2\,PhSO_2NCl_2 \longrightarrow 2\,ArS(=NSO_2Ph)Cl + Cl_2.$$

The formation of arenesulfonamides as by-products makes it difficult to isolate the iminosulfinyl chlorides. Consequently the preparation of iminosulfinyl chlorides from disulfides and *N*-dichloro-compounds is more convenient for preparative purposes.[411-417]

$$RSSR + 2\,R^1NCl_2 \xrightarrow[-Cl_2]{} 2\,RS(=NR^1)Cl$$

R = Alk, Ar; R^1 = $ArSO_2$, ArCO, Bu^t.

3. Preparation of sulfur(VI) compounds

a. Preparation of sulfonic acids

Thiols are readily converted to sulfonic acids by the action of strong oxidising agents.[77] A number of methods for preparing sulfonic acids have been developed on the basis of this reaction.

$$RSH \xrightarrow{Ox} RSO_3H$$

R = Alk, Ar, Het.

The oxidation of thiols to sulfonic acids takes place via a number of stages in which the intermediate compounds are disulfides, sulfinic and sulfonic acids. For example, the oxidation of thiols by the $Ti^{III}-H_2O_2$ system or Ce^{IV} salts leads to the successive generation of thiyl, sulfinyl and sulfonyl radicals, from which the final products are formed.[4] In biological systems inclusion of sulfur in the metabolism occurs starting with the oxidation of cysteine to alanine-3-sulfinic acid, which is subsequently converted to a β-sulfenylpyruvate, sulfite ions, and finally sulfate ions.

A method for preparing aliphatic sulfonic acids is based on the addition of thiols to alkenes followed by oxidation of the resultant thioethers by hydrogen peroxide in acetic acid.[4]

$$RCH{=}CH_2 + AcSH \xrightarrow{h\nu} RCH_2CH_2SAc \xrightarrow{H_2O_2}$$
$$\longrightarrow RCH_2CH_2SO_3H$$

b. Preparation of sulfonyl chlorides

Oxidative chlorination of aromatic and heterocyclic thiols with chlorine in glacial acetic acid gives the corresponding sulfonyl chlorides.[77]

$$RSH + Cl_2 \xrightarrow[-HCl,\,MeCOCl]{MeCOOH} RSO_2Cl$$

Oxidative chlorination of aliphatic thiols occurs in aqueous solution.[418]

$$RSH + 3\,Cl_2 + 2\,H_2O \longrightarrow RSO_2Cl + 5\,HCl$$

Oxidative chlorination of thioglycolic acid in concentrated hydrochloric acid gives dichloromethanesulfonyl chloride.[419]

$$HO_2CCH_2SH + Cl_2 \xrightarrow{HCl\,+\,H_2O} HO_2CCH_2SO_2Cl \xrightarrow[-2\,HCl]{Cl_2}$$
$$\longrightarrow [HO_2CCCl_2SO_2Cl] \xrightarrow[-CO_2]{} CHCl_2SO_2Cl$$

In this review an attempt has been made to demonstrate the great synthetic potentialities for fine-organic synthesis which lie hidden in a class of organosulfur compounds that is, on the face of it, just ordinary, viz. thiols. In the review thiols are discussed only as synthons although there are other reactions involving thiols which have no synthetic value but play an important role in various fields of human activity (e.g. the purification of petroleum from sulfur compounds etc.).

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