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REVIEW

Reactions of Thiols

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Abstract—Published data on the reactivity of thiols, specifically C-, N-, P-, and S-sulfanylation reactions, halogenolysis of S–H bond, dealkylation, and oxidation, are reviewed.

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1. INTRODUCTION

All chemical processes occurring with thiols may be divided into the following groups with respect to the character of changes in their molecules: reactions involving cleavage of the S–H bond; reactions involving cleavage of the C–S bond; reactions accompanied by change of the oxidation state of the sulfur atom; and heterocyclizations. It should be emphasized that each of these groups includes a variety of transformations which cannot be covered to a sufficient extent in the framework of a single paper; therefore, the present review deals only with the first three groups of thiol reactions.

Ivan Koval' was born in 1942 in Podgorodnoe village, Dnepropetrovsk region. In 1967 he graduated from the Dnepropetrovsk Institute of Chemical Technology; Candidate of chemical sciences since 1970, Doctor of chemical sciences since 1987; In 1995, I. Koval' was elected a Full Member of the Ukrainian Academy of Technology. I. Koval' is now head of the Department of Chemical Technology of High-Molecular Compounds at the Ukrainian State University of Chemical Technology, Dnepropetrovsk, Ukraine.

Fields of scientific interest: organoelement chemistry and chemistry of high-molecular compounds. I. Koval' discovered, developed methods for generation, and thoroughly studied properties of α-sulfenyl N-centered anions. He is author of more than 200 publications, including 20 reviews on modern problems of organoelement chemistry.

Reactions involving cleavage of the S–H bond are especially diverse. The ease of dissociation of the S–H bond in thiols is directly related to its energy which is estimated at 82–94 kcal/mol [1]. Depending on the conditions and thiol nature, heterolytic dissociation of the S–H bond to give thiolate anion or sulfanyl cation or homolytic dissociation with formation of sulfanyl radicals can occur, and these species can directly participate in various transformations.

Processes accompanied by cleavage of the S–H bond primarily include those resulting in introduction of an RS fragment into organic molecules. Such reactions are generically called *sulfanylation* (*thiylation*). Depending on the bond being formed, C-, N-, P-, S-, and Si-sulfanylation may be distinguished. In the recent years, sulfanylation reactions have been exten-

sively used in preparative organic chemistry and chemistry of natural compounds. These reactions underlie a number of preparative methods for the synthesis of sulfides [2, 3], disulfides [4, 5], and sulfenamides [6, 7], including biologically active compounds [8], as well as for introduction of acid-labile protecting groups into molecules of sulfur-containing amino acids and proteins [9, 10] and deprotection [11–15].

2. C-SULFANYLATION

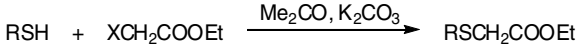
C-Sulfanylation is based primarily on replacement of halogen atoms and other functional groups at a carbon atom by RS group, addition of thiols at multiple bonds of unsaturated compounds, and opening of unstable rings by the action of thiols.

2.1. Replacement of Halogen at a Carbon Atom by RS Group

Replacement of a halogen atom by an RS group occurs in reactions of thiols with various halogen derivatives. Replacement of a halogen atom at a saturated carbon atom by an RS group has long been known and extensively studied; as a rule, it follows a bimolecular mechanism, and *d* orbitals of the sulfur atom participate in stabilization of the transition state. Several procedures for performing such reactions have been developed. The most widely used version implies heating of a mixture of appropriate thiol and halogen derivative in a polar solvent (aqueous alcohol, alcohol, acetone, DMF, DMSO, etc.) in the presence of an alkali. For example, benzenethiol [16, 17], 1,3-benzothiazole-2-thiol [18], benzimidazole-2-thiol [18], and 1,3-benzoxazole-2-thiol [18] were alkylated with ethyl chloroacetate, while 5-methyl-1,3,4-thiadiazole-2-thiol was alkylated with ethyl bromoacetate [19] with a view to obtain new antimicrobial agents (Scheme 1). The reactions were carried out by heating the reactants in boiling acetone in the presence of K_2CO_3. Chloromethylation of 1,3-benzoxazole-2-thiol was performed under analogous conditions [20].

The reaction of bis(2-chlorocyclohexyl) sulfide with benzenethiol gave bis(2-phenylsulfanylcyclohexyl) sulfide as a mixture of stereoisomers [21].

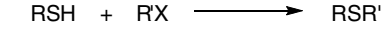
Scheme 1.



R = Ph, 1,3-benzothiazol-2-yl, 1,3-benzoxazol-2-yl, 1*H*-benzimidazol-2-yl, 5-methyl-1,3,4-thiadiazol-2-yl; X = Cl, Br.

A number of symmetric and unsymmetric sulfides were synthesized using acetone, dimethylformamide, or their mixture as solvent in the presence of K_2CO_3 [22–24] (Scheme 2). The reactions were activated by ultrasonic [22] or microwave irradiation [23].

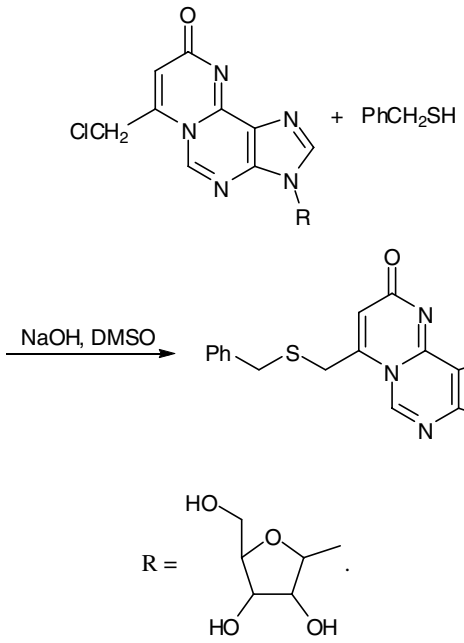
Scheme 2.



R = Bu, $PhCH_2$, $HOCH_2CH_2$, Ph, 4-ClC_6H_4, 2-HSC_6H_4; R' = Pr, *i*-Pr, Bu, $PhCH_2$, $C_{12}H_{25}$; X = Cl, Br.

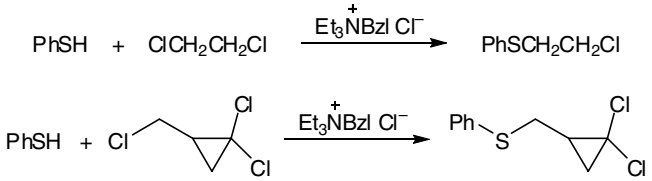
Sodium hydroxide is used very frequently as hydrogen halide acceptor, e.g., in the replacement of the chlorine atom in the chloromethyl fragment of nucleosides by benzylsulfanyl group [25] (Scheme 3).

Scheme 3.



In some cases, aqueous–alcoholic [26] or aqueous solutions [27–30] of NaOH are used instead of solid alkali, and sulfanylation in aqueous medium is carried out in the presence of phase-transfer catalysts [27, 28, 30]. Replacement of one chlorine atom in 1,2-dichloroethane [27] and 1,1-dichloro-2-chloromethylcyclo-

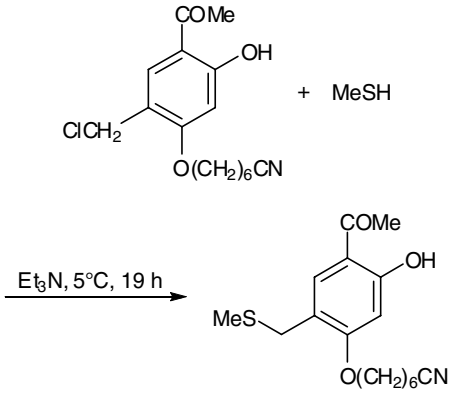
Scheme 4.



propane [28] by phenylsulfanyl group was performed in aqueous–alcoholic medium in the presence of benzyltriethylammonium chloride (Scheme 4). Kannan et al. [31] used modified bentonite clays to catalyze reactions of thiols with benzyl chlorides.

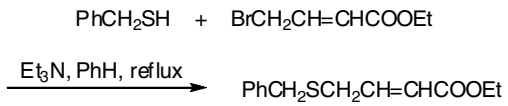
According to the second procedure for replacement of a halogen atom at a saturated carbon atom by RS group, reactions of thiols with halogen derivatives are performed in anhydrous organic solvents in the presence of organic bases, such as triethylamine, pyridine, etc. For instance, the benzylic chlorine atom in 7-(4-acetyl-2-chloromethyl-5-hydroxyphenoxy)heptanenitrile was replaced by methylsulfanyl group in chloroform in the presence of triethylamine [32] (Scheme 5).

Scheme 5.

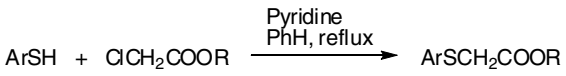


Likewise, the bromine atom in ethyl 4-bromobut-2-enoate was replaced by benzylsulfanyl group in the presence of triethylamine [33] (Scheme 6), while the chlorine atom in quinolin-8-yl chloroacetate was replaced by arylsulfanyl groups in the presence of pyridine [34] (Scheme 7).

Scheme 6.



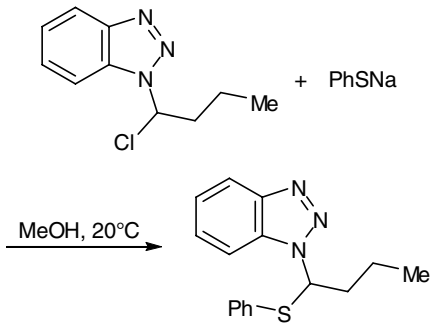
Scheme 7.



R = Quinolin-8-yl; Ar = 4-MeC_6H_4, 4-ClC_6H_4.

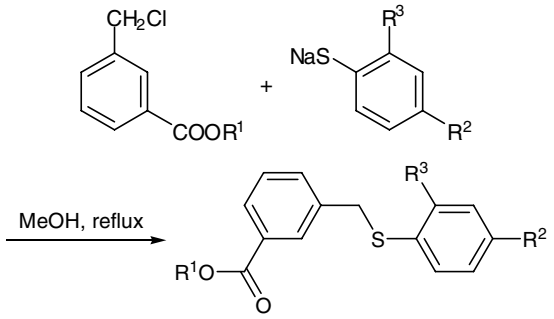
The third version makes use of alkali metal thiolates that are brought into reaction with halogen derivatives, as a rule in alcoholic medium. An example is the synthesis of 1-(1-phenylsulfanylbutyl)-1*H*-benzotriazole by reaction of sodium benzenethiolate with 1-(1-chlorobutyl)-1*H*-benzotriazole in methanol [35] (Scheme 8).

Scheme 8.



Replacement of the chlorine atom in methyl and ethyl 3-chloromethylbenzoates by arylsulfanyl groups was performed under analogous conditions [36] (Scheme 9).

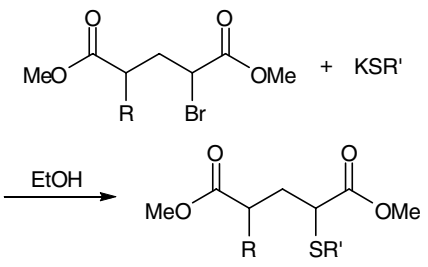
Scheme 9.



R^1 = Me, Et; R^2 = H, Br, Cl, Me, Et, MeO; R^3 = H, HOCO, MeOCO, EtOCO.

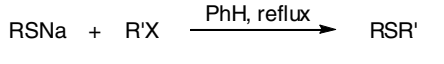
An important step in the synthesis of 4-R-sulfanyl derivatives of glutamic acid [37] is the reaction of the corresponding bromo derivative with potassium thiolates in alcoholic medium (Scheme 10). Halogen atoms in polyfluorohaloalkanes were replaced by RS groups by heating with the corresponding sodium

Scheme 10.



R = Phthalimido; R' = Me, C_6H_{13}, etc.

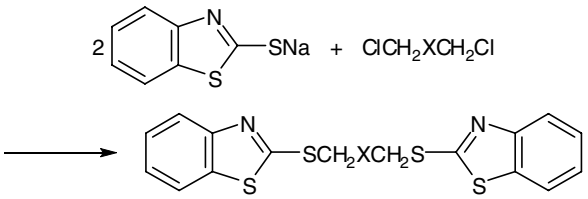
Scheme 11.



R = $Me_{3-m}(MeO)_mSi(CH_2)_n$ (m = 2, 3, n = 1–3); R' = $H(CF_2)_2CH_2$, $H(CF_2)_4CH_2$, $H(CF_2)_6CH_2$; X = Cl, Br, I.

thiolates in boiling benzene [38] (Scheme 11). Mesropyan et al. [39] reported on the synthesis of bis-sulfides from sodium 1,3-benzothiazole-2-thiolate and bis-chloromethyl derivatives of aromatic hydrocarbons. Reactant mixtures were heated in DMF at 130–135°C (Scheme 12).

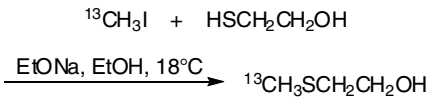
Scheme 12.



X = *p*-C_6H_4; *p*-$C_6H_4C_6H_4$-*p*; *p*-$C_6H_4CH_2C_6H_4$-*p*.

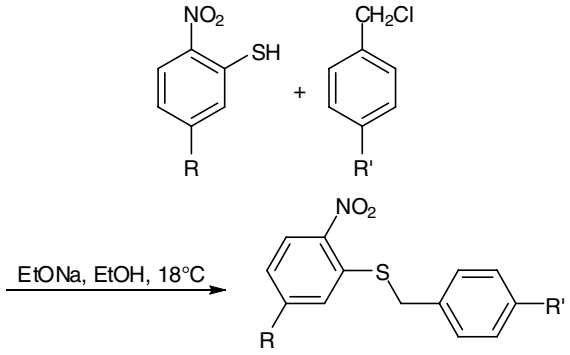
Reactions of thiols with halogen derivatives in alcoholic medium in the presence of metal alkoxides may be regarded as a modification of the third procedure. Taber and Meagley [40] described the synthesis of 2-chloroethyl [^{13}C]-methyl sulfide in which one step was the reaction of [^{13}C]-methyl iodide with 2-sulfanylethanol in ethanol in the presence of sodium ethoxide (Scheme 13).

Scheme 13.



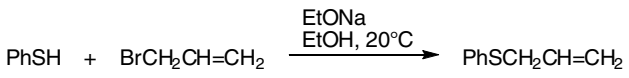
Ethanolic sodium ethoxide was used to effect substitution of the chlorine atom in benzyl chloride and its derivatives by arylsulfanyl groups [41] (Scheme 14), as well as alkylation of benzenethiol with allyl bromide [42] (Scheme 15). A number of 4-R-2-(R'-methylsulfanyl)-5-phenyl-3,4-dihydro-2*H*-1,2,4-triazole-3-thiones possessing fungicide activity were synthesized by heating the corresponding chloromethyl derivatives with thiols in a boiling solution of sodium ethoxide in ethanol [43] (Scheme 16). Replacement of the chlorine atom in bicyclo[4.3.0]nonane derivative by phenylsulfanyl group was carried out in methanol in the presence of potassium *tert*-butoxide [44] (Scheme 17). Selective replacement of the bromine atom in 1-bromo-3-chlorocyclobutane by triphenylmethylsulfanyl group also occurs in methanol in the presence of sodium methoxide [45] (Scheme 18).

Scheme 14.

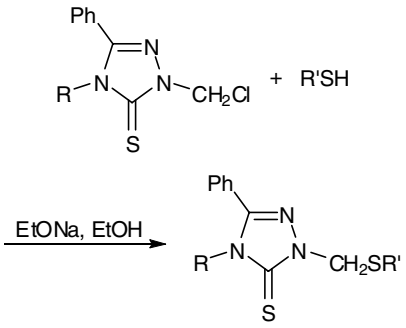


R = H, Cl; R' = H, Me, MeO.

Scheme 15.

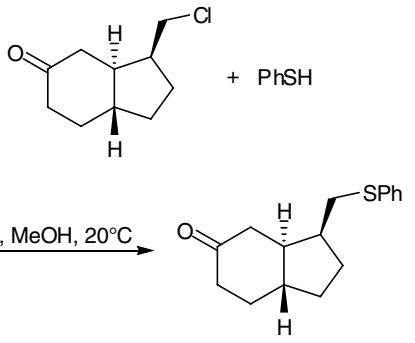


Scheme 16.

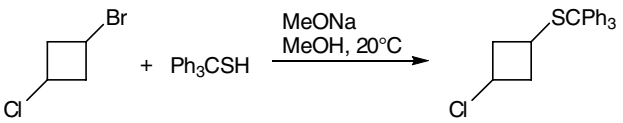


R = Me, Ph; R' = Pr, *i*-Pr, Ph, 4-ClC_6H_4, C_6H_{11}, 2-pyridyl, 1,3-benzoxazol-2-yl, 1,3-benzothiazol-2-yl.

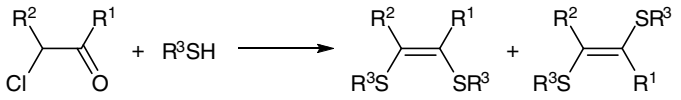
Scheme 17.



Scheme 18.

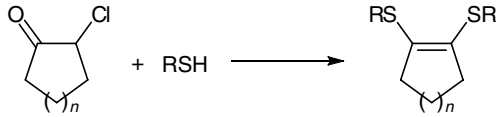


Scheme 19.



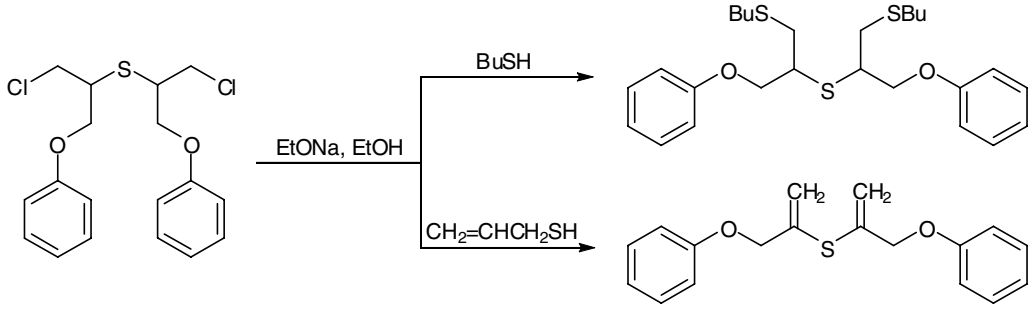
R^1 = Me; R^2 = H, Me; R^3 = Et, Pr, Bu.

Scheme 20.



R = Et, Bu; *n* = 1, 2.

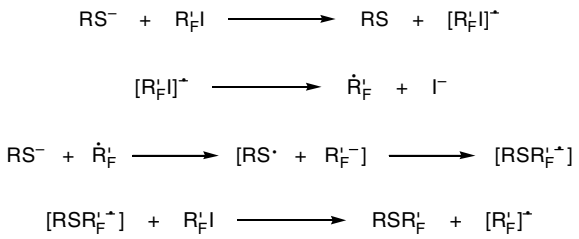
Scheme 21.



If a halogen derivative contains other functional groups capable of reacting with thiols, nucleophilic substitution can be accompanied by side processes leading to different products. Mursakulov et al. [46] examined reactions of α-chloro ketones with alkanethiols and found that the product structure depends on the nature of initial α-chloro ketone. Acyclic α-chloro ketones gave rise to mixtures of isomeric *cis*- and *trans*- bis(alkylsulfanyl)alkenes [46] (Scheme 19), while only *cis*-1,2-bis(alkylsulfanyl)cycloalkenes were obtained from cyclic α-chloro ketones (Scheme 20). The authors presumed [46] that the first stage of this process is nucleophilic replacement of chlorine by alkylsulfanyl group to give alkylsulfanyl ketones; addition to the latter of the second thiol molecule leads to the corresponding alkylsulfanyl-substituted alcohols which lose water molecule under acidic conditions to form the final products. The nature of thiol can also affect the product structure, as illustrated by Scheme 21 [47]. It is seen that the reaction with butane-1-thiol gives the corresponding nucleophilic substitution product and that unsaturated sulfide is formed in the reaction with prop-2-ene-1-thiol.

A specific case of nucleophilic replacement of a halogen atom at a saturated carbon atom by RS group is the reaction of perfluoroiodoalkanes with thiols. The reaction is initiated by UV irradiation, and it follows $S_{RN}1$ radical ion mechanism [1, 48, 49] (Scheme 22).

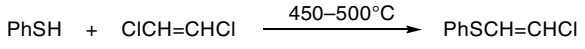
Scheme 22.



R = Alk, Ar, $EtOC(O)CH_2$; R' = C_3F_7, C_8F_{17}.

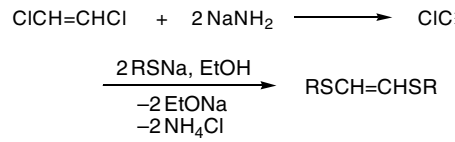
Some systems, e.g., I_2–SO_2, facilitate perfluoroalkylation of thiols [50]. Replacement of a halogen atom at an unsaturated carbon atom (in olefins and acetylene derivatives) by RS group is a relatively rare case, for such halogen derivatives are inert toward thiols or thiolate ions. As a rule, fairly severe conditions are necessary to enable these reactions to occur, and they follow either radical or elimination–addition mechanism. For example, benzenethiol reacts with 1,2-dichloroethene in the gas phase at 450–500°C according to radical mechanism to produce a mixture of *cis*- and *trans*-1-chloro-2-phenylsulfanylethylenes at a ratio of 1:1 [51] (Scheme 23).

Scheme 23.



(*E*)-1,2-Dichloro-1-phenylsulfanylethylene was obtained in 63% yield by treatment of 1,1,2-trichloroethylene with benzenethiol in alcoholic medium in the presence of sodium ethoxide on heating for 12 h under reflux [52]. Bjorlo et al. [53] described a one-pot two-step synthesis of (*Z*)-bis(methylsulfanyl)- and (*Z*)-bis(ethylsulfanyl)ethenes, where one step involved replacement of chlorine at an unsaturated carbon atom by RS group (Scheme 24).

Scheme 24.

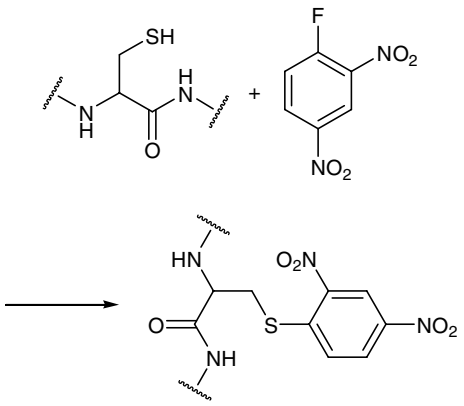


R = Me, Et.

Propane-1,3-dithiol and hexane-1,6-dithiol react with hexachlorobuta-1,3-diene in alcoholic alkali to give mixtures of products as a result of nucleophilic substitution of the terminal chlorine atoms [54].

Much attention is given to halogen replacement by RS groups in the benzene ring of aromatic hydrocarbons. These reactions have found wide application in bioorganic chemistry for the introduction of protecting groups and various labels into peptide and protein molecules possessing HS groups. The most frequently used reagent is 1-fluoro-2,4-dinitrobenzene [9] (Scheme 25).

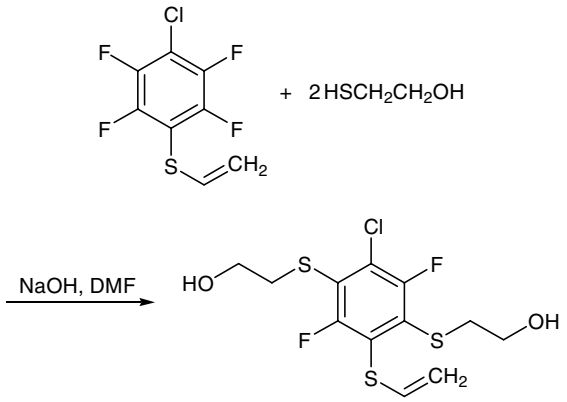
Scheme 25.



Rybakova et al. [55] previously reviewed methods for replacement of halogen atoms in an aromatic ring by RS groups; the review covered the relevant literature till 1990; therefore, only more recent publications are considered in the present review. Replacement of a halogen atom in aryl halides by RS group is facilitated when the aromatic ring contains strong electron-withdrawing groups (such as NO_2, CN, etc.) in the *ortho* or *para* position with respect to the halogen atom, i.e., when the latter is activated [56, 57]. In these cases, the reactions are carried out by heating an appropriate aryl halide with sodium thiolate in alcoholic medium. The sulfanylation process follows the S_N2Ar bimolecular mechanism involving formation of intermediate σ-complex which is stabilized due to participation of the electron-withdrawing group and *d* orbitals of the sulfur atom.

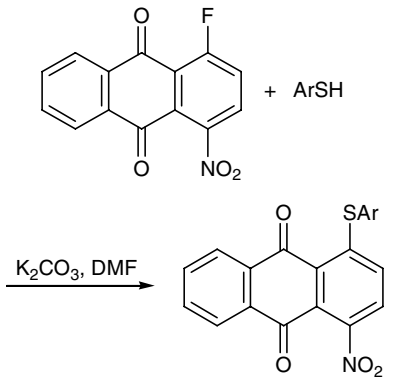
The reactivity of activated aryl halides toward thiolate ions depends on the halogen nature, and it weakens in the series F > Br > Cl [55]. The rates of replacement of Br, I, and Cl differ insignificantly, while the rate of replacement of fluorine is greater by about two orders of magnitude. These data indicate that polarization of the carbon–halogen bond (more exactly, electron deficiency of the carbon atom attached to halogen) is the determining factor in this process. Therefore, the reaction of 6-chloro-1,2,4,5-tetrafluoro-3-vinylsulfanylbenzene with 2-sulfanylethanol in DMF in the presence of NaOH at room temperature results in replacement of two fluorine atoms rather than of the chlorine atom [58] (Scheme 26).

Scheme 26.



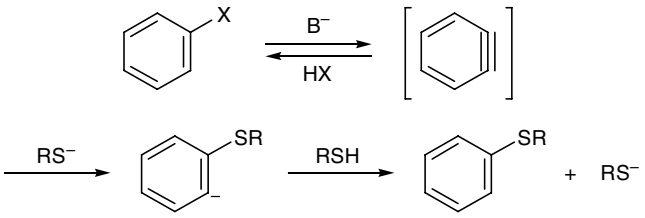
Reactions of 4-fluoro-1-nitroanthraquinone with arenethiols also involve replacement of the fluorine atom by arylsulfanyl group [59] (Scheme 27). Nonactivated aryl halides [60–63] react with thiolate ions under more severe conditions (elevated temperature, strong base) according to the elimination–addition mechanism (Scheme 28). In some cases, the process was accelerated using copper compounds (Cu, Cu_2O,

Scheme 27.



Ar = Ph, 4-$O_2NC_6H_4$.

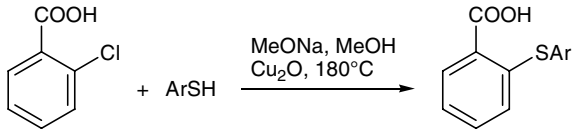
Scheme 28.



X = Cl, Br, I, F; R = Alk, Ar, Ht; B^- = MeO^-, *t*-BuO^-, NH_2^-.

CuBr, etc.) as catalyst. For instance, the chlorine atom in 2-chlorobenzoic acid was replaced by arylsulfanyl groups by heating the reactants in methanol in the presence of sodium methoxide and copper(I) oxide [61] (Scheme 29).

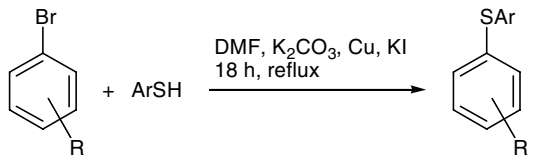
Scheme 29.



Ar = 2-MeC_6H_4, 4-MeC_6H_4.

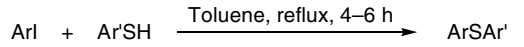
The system DMF–K_2CO_3–Cu–KI was used to replace the bromine atom in 2- and 4-bromotoluenes by ArS groups [61] (Scheme 30). Palomo et al. [63] synthesized a series of unsymmetric diaryl sulfides by reactions of the corresponding aryl iodides with arenethiols in boiling toluene (reaction time 4–6 h) in the presence of phosphazenes and copper(I) bromide (Scheme 31). According to the authors [63], the yield of diaryl sulfides was 91 to 100%.

Scheme 30.



R = 2-Me, 4-Me; Ar = 2-$HOCOC_6H_4$.

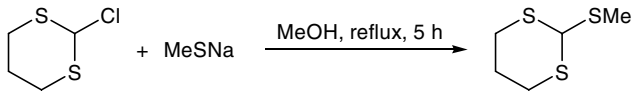
Scheme 31.



Ar = Ph, 3,5-$Me_2C_6H_3$, 2,4-$Me_2C_6H_3$; Ar' = 4-ClC_6H_4, 4-MeC_6H_4.

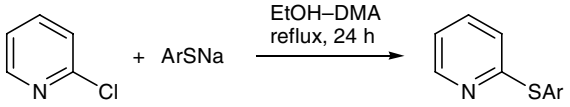
A relatively large number of studies [64–70] deal with nucleophilic substitution of halogens in various heterocyclic compounds by RS groups; these reactions are usually performed to obtain new biologically active substances. Mitsudera et al. [71] synthesized 5-methylsulfanyl-1,3-dithiane (an analog of charatoxin) by treatment of 5-chloro-1,3-dithiane with sodium methanethiolate in boiling methanol over a period of 5 h (Scheme 32).

Scheme 32.



More severe conditions are necessary to replace a halogen atom in pyridine ring by RS group. For example, 2-chloropyridine was converted into 2-arylsulfanylpyridines by heating with the corresponding sodium arenethiolate in ethanol–*N*,*N*-dimethylacetamide for 24 h [72] (Scheme 33).

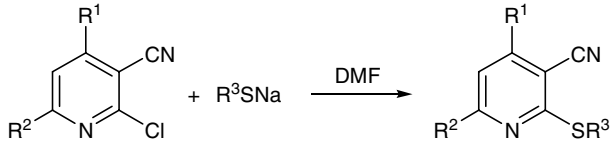
Scheme 33.



Ar = Ph, 4-MeC_6H_4.

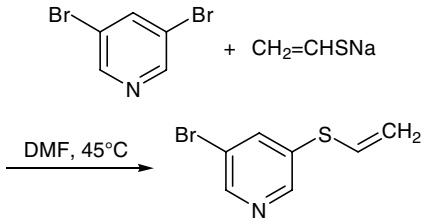
If an electron-acceptor group is present in the pyridine ring together with halogen atom, replacement of the latter by RS group occurs under milder conditions. 2-Chloropyridine-3-carbonitrile [73] reacted with sodium thiolates in the presence of sodium methoxide or KOH at 20°C (3–4 h), while analogous reactions with 6-R^2-4-R^1-2-chloropyridine-3-carbonitrile [74] required heating for 12–14 h at 60–65°C (Scheme 34). The replacement of one bromine atom in 3,5-dibromopyridine by vinylsulfanyl group to give 3-bromo-5-(vinylsulfanyl)pyridine was effected under relatively mild conditions [75] (Scheme 35). The reaction was accompanied by formation of 3-bromo-5-(but-1-en-1-

Scheme 34.



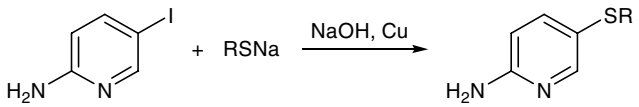
$R^1 = R^2 = H$, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$; R^3 = Pr, Bu, $EtOCOCH_2$.

Scheme 35.



ylsulfanyl)pyridine. The iodine atom in 5-iodopyridin-2-amine is replaced by RS groups only in the presence of copper powder [76] (Scheme 36).

Scheme 36.

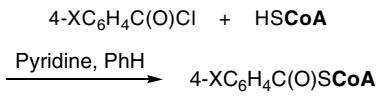


R = Me, Pr, Ph.

In the reaction of 4-chloro-3-nitrocoumarin with an equivalent amount of phenylmethanethiol, 4-benzylsulfanyl-3-nitrocoumarin was formed in quantitative yield, while the reaction with 2 equiv of phenylmethanethiol gave 3,4-bis(benzylsulfanyl)coumarin [77]. Many publications describe replacement by RS groups of halogen atoms in heterocyclic fragments of various natural compounds. Sulfanylation of 8-bromoadenosine [78] and steroids [79] with sodium methanethiolate and substitution of bromine and chlorine atoms in some mono- [80, 81] and disaccharides [82] by PhS and $HS(CH_2)_3S$ groups were reported.

Replacement of halogen atoms in acyl halides by RS groups has been studied in sufficient detail; these reactions usually follow S_N2 bimolecular mechanism. In the recent years, reactions of acyl halides with thiols have been widely used in the synthesis and modification of various natural compounds. With a view to elucidate the mechanism of action of 4-chlorobenzoyl coenzyme A dehalogenase, Crooks and Copley [83] synthesized a series of CoA *S*-esters by acylation of sulfanyl groups in the latter with acyl chlorides (Scheme 37).

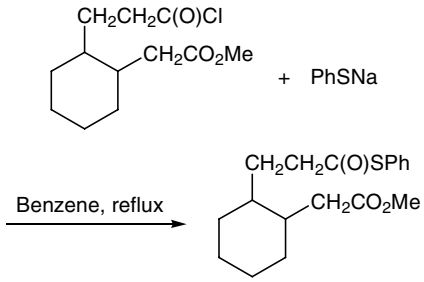
Scheme 37.



X = Cl, Br, F.

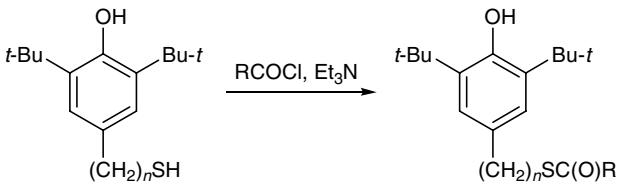
Kumar et al. [84] described a simple and convenient synthesis of 1-benzothiopyran-4-ones; an important step in the synthetic sequence was replacement of chlorine in acyl chlorides by the 2-sulfanylbenzoic acid residue. A multistep synthesis of steroid analogs included replacement of the chlorine atom in 3-(2-methoxycarbonylmethylcyclohexan-1-yl)propionyl chloride by phenylsulfanyl group [85] (Scheme 38).

Scheme 38.



A number of sulfides exhibiting antioxidant activity toward animal fats were synthesized by treatment of fatty acid chlorides with fatty–aromatic thiols in the presence of triethylamine [86] (Scheme 39).

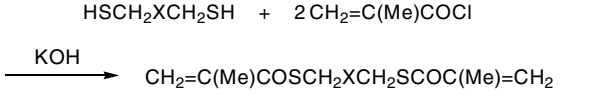
Scheme 39.



R = Me, Bu, C_5H_{11}; n = 2–4.

Bis-sulfides interesting as potential biologically active substances were obtained from dithiols and methacryloyl chloride in the presence of potassium hydroxide and a phase-transfer catalyst [87] (Scheme 40). Carboxylic acid anhydrides are rarely used as acylating agents toward thiols [88, 89].

Scheme 40.

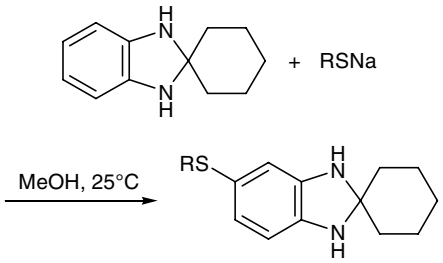


X = CH_2, $CH_2OCH_2CH_2$, $CH_2(CH_2CH_2O)_2$, $CH_2SCH_2CH_2$.

2.2. Replacement of Other Atoms and Functional Groups by RS Group

Replacement of hydrogen by RS group is a fairly rare reaction. Hazelton et al. [90] described substitution of 5-H in 2,3-dihydro-1*H*-spiro[benzimidazole-2,1'-cyclohexane] by RS group (Scheme 41); in the reaction with 2 equiv of sodium thiolate, hydrogen replacement in position *6* is also possible.

Scheme 41.

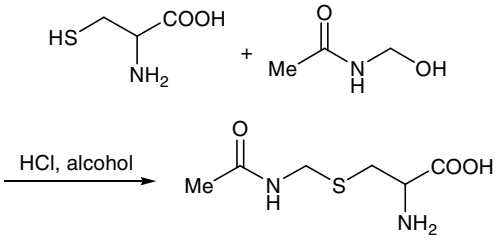


R = Pr, *t*-Bu, Ph, 2-pyridyl.

3-Acetyl-1-methoxyindole reacted with sodium methanethiolate to give the corresponding 2-methylsulfanyl derivative in 93% yield [91]. Replacement of two hydrogen atoms in the quinoid ring of the antitumor antibiotic Quinocarcin by two RS groups was reported [92]. The reaction was carried out in aqueous acetonitrile in the presence of an acetate buffer, followed by treatment with Fremy's salt. Obviously, the substitution process followed the addition–elimination (oxidation) pattern.

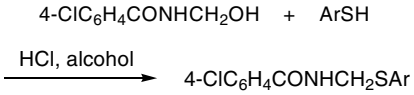
Replacement of various functional groups by RS moieties was reported much more frequently. Primarily, many examples of hydroxy group substitution were described. Several procedures were developed for this purpose. The first of these is based on reactions of hydroxy compounds with thiols in the presence of a catalyst. *S*-Acetylaminomethylcysteine (which is widely used in peptide syntheses) was prepared from cysteine and acetamide in alcoholic medium in the presence of hydrogen chloride [9] (Scheme 42).

Scheme 42.



Replacement of the hydroxy group in 4-chloro-*N*-(hydroxymethyl)benzamide by arylsulfanyl groups was performed under analogous conditions [93] (Scheme 43).

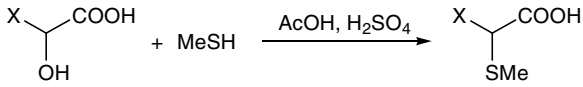
Scheme 43.



Ar = 3-MeC_6H_4, 3-$MeOC_6H_4$.

Repin et al. [94] reported on the replacement of the α-hydroxy group in α-amino acid fragments of peptides by methylsulfanyl group in acetic acid in the presence of concentrated sulfuric acid (Scheme 44). Presumably, the initial step is formation of α-amino acid ester which then reacts with methanethiol to give the final product.

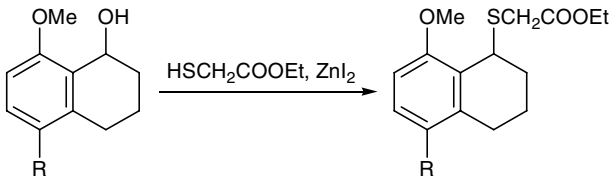
Scheme 44.



X is a peptide residue.

The hydroxy group in 1-hydroxy-5-R-8-methoxytetrahydronaphthalene was replaced by ethoxycarbonylmethylsulfanyl group in the presence of zinc(II) iodide [95] (Scheme 45). Boron trifluoride–ether complex was also used to catalyze replacement of the hydroxy group in fatty–aromatic [96, 97] and allyl alcohols [98] by RS group.

Scheme 45.

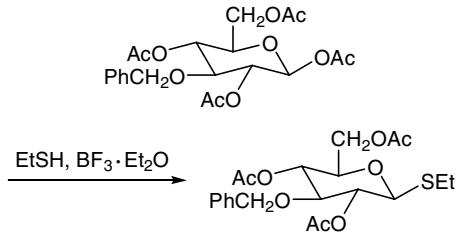


R = H, MeO.

The second procedure for the replacement of OH group by RS includes preliminary acylation of hydroxy compound with acyl chlorides or carboxylic acid anhydrides, followed by replacement of the acyloxy group by RS. This version is especially widely used in the carbohydrate chemistry, in particular in the synthesis of thioglycosides. The second step of the process, i.e., replacement of acyloxy group by sulfanyl, is usually carried out in the presence of a catalyst such as boron

trifluoride–ether complex. 1,2,4,6-Tetra-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranose was thus converted into ethyl 2,4,6-tri-*O*-acetyl-3-*O*-benzyl-1-thio-β-D-glucopyranoside [99] (Scheme 46).

Scheme 46.

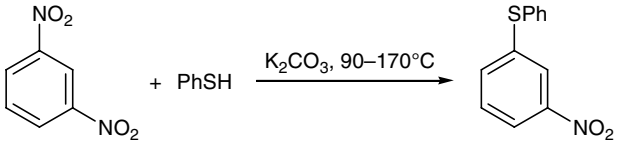


Thioglycosylation of other pyranosides was performed under similar conditions [100–103]. The acetoxy group in 3,4-di-*O*-acetyl-L-rhamnal was replaced by acetylsulfanyl group [104], and the benzoyloxy group in methyl benzoate was replaced by alkyl(aryl)sulfanyl groups [105] in the absence of a catalyst.

According to the third procedure for the replacement of hydroxy group by R-sulfanyl, the substrate is initially treated with sulfonyl chlorides or sulfonic acid anhydrides to obtain the corresponding sulfonate, and the latter is brought into reaction with thiols or sodium thiolates. This version was widely used in syntheses and transformations of antibiotics [106], moth pheromones [107, 108], nucleosides [109], amino acids [110–112], carbohydrates [113, 114], and other natural compounds [115–117].

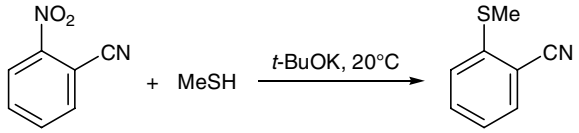
Replacement of an activated nitro group in an aromatic ring by RS group has been studied relatively well [55]. This reaction occurs generally in polar organic solvents according to the S_N2Ar mechanism. One nitro group in *m*-dinitrobenzene is readily replaced by phenylsulfanyl group in dimethylformamide or dimethyl sulfoxide in the presence of potassium carbonate on heating to 90–170°C [118] (Scheme 47).

Scheme 47.

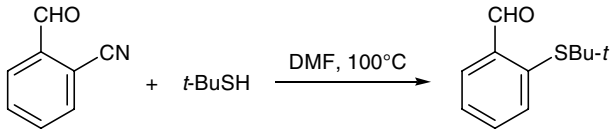


Likewise, 2-nitrobenzonitrile reacts with methanethiol in dimethyl sulfoxide in the presence of potassium *tert*-butoxide to give 2-methylsulfanylbenzonitrile [119] (Scheme 48). 2-*tert*-Butylsulfanylbenzaldehyde was obtained in 72% yield by heating 2-nitrobenzaldehyde with 2-methylpropane-2-thiol in dimethylformamide [120] (Scheme 49).

Scheme 48.

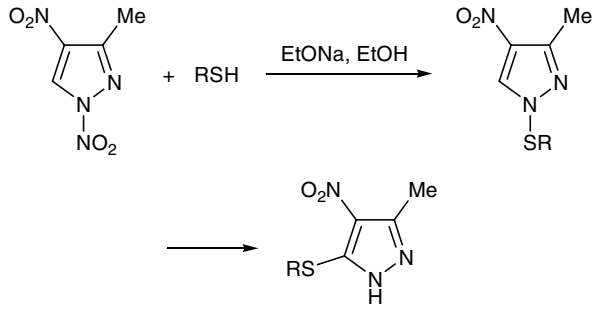


Scheme 49.



2,4,6-Trinitrotoluene reacted with alkane- [121] or arenethiols [122] in dipolar aprotic solvents (dimethylformamide, dimethyl sulfoxide) containing LiOH, KOH, or K_2CO_3); as a result, the corresponding 2-alkyl-(aryl)sulfanyl-4,6-dinitrotoluenes were formed via selective replacement of the *ortho*-nitro group. In the reaction with 2 equiv of thiol, both *ortho*-nitro groups can be replaced [121]. Abramov et al. [123] synthesized 4-(*m*-carboran-9-ylsulfanyl)phthalonitrile in 62.5% yield from the corresponding thiol and 4-nitrophthalonitrile in DMF in the presence of K_2CO_3 [123]. The *N*-nitro group in 3-methyl-1,4-dinitropyrazole was replaced by phenyl- and ethoxycarbonylmethylsulfanyl groups, and the subsequent isomerization gave the corresponding 5-sulfanyl derivatives [124] (Scheme 50).

Scheme 50.



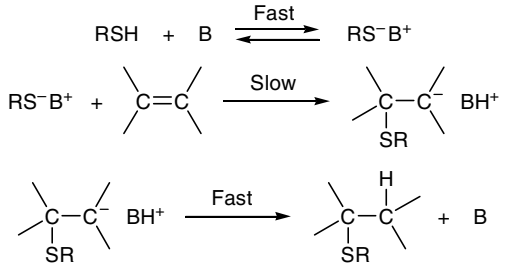
Replacements of alkyl(aryl)sulfonyl [125, 126], alkoxy [127, 128], trimethylsilyl [129], allylselanyl [130], and trimethylammonio groups [131] by RS moieties have also been reported, but such reactions are fairly rare.

2.3. Addition of Thiols at Multiple Bonds of Unsaturated Compounds

Thiols are capable of adding at double C=C bonds of unsaturated compounds to give various sulfides. Depending on the reaction conditions, the addition process can follow nucleophilic, electrophilic, or

radical mechanism. Nucleophilic addition of thiols to unsaturated compounds is a more common reaction; as a rule, it is promoted by base catalysts which favor formation of thiolate ions. The rate-determining stage is the addition of thiolate anion to sp^2-hybridized carbon atom [9] (Scheme 51).

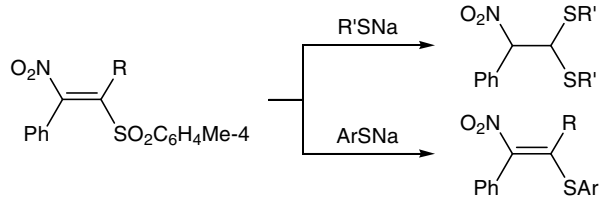
Scheme 51.



Such organic bases as triethylamine [132], diisopropylamine [133], and piperidine [134, 135] and inorganic sodium [136] and potassium carbonates [137] are the most frequently used catalysts. In some cases, the reactions are performed with sodium thiolates [138] rather than with the corresponding thiols. Thiols add relatively readily at polarized conjugated bond systems in unsaturated aldehydes [139], ketones [132, 140], esters [141, 142], amides [137] and imides [143], vinyl [144] and divinyl sulfones [145], and 1,3-dinitrodienes [146].

1-Nitro-2-sulfonylalkenes react with arenethiolates to give products of replacement of the sulfonyl group, while in reactions with alkanethiolates nitro dithioacetals are formed as a result of subsequent addition of the second thiol molecule [147] (Scheme 52).

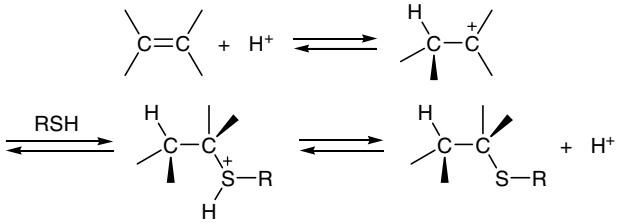
Scheme 52.



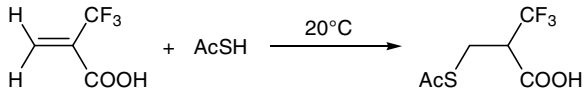
R = H, Ph; R' = Et, $C_{12}H_{25}$; Ar = 4-MeC_6H_4, 4-ClC_6H_4.

Electrophilic addition of thiols at C=C bonds of unsaturated compounds occurs in acidic medium and involves intermediate formation of carbocationic species [9] (Scheme 53). Here, the nature of both thiol and unsaturated substrate is important. Vasil'eva et al. [148] studied electrophilic addition of various thiols at the C=C bond of α- and β-trifluoromethyl-substituted acrylic acids. The addition of thioacetic acid to α-trifluoromethylacrylic acid was accompanied by heat evolution, and the product was 3-acetylsulfanyl-2-trifluoromethylpropionic acid (Scheme 54).

Scheme 53.

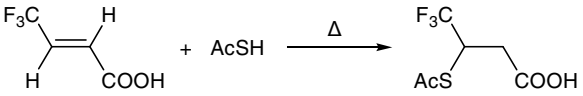


Scheme 54.



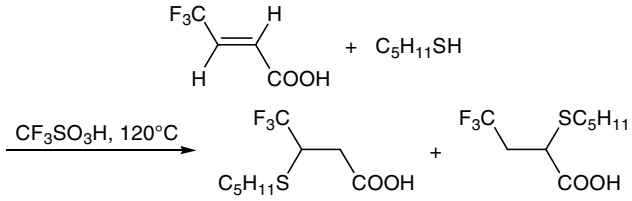
Thioacetic acid reacted with β-trifluoromethylacrylic acid on heating with exceptional regioselectivity, yielding the corresponding β-acetylsulfanyl-substituted derivative (Scheme 55).

Scheme 55.



Addition of phenylmethanethiol at the C=C bond of α-trifluoromethylacrylic acid occurs only at 100°C to give β-benzylsulfanyl derivative, while β-trifluoromethylacrylic acid does not react with phenylmethanethiol even on prolonged heating. The reaction of β-trifluoromethylacrylic acid with pentane-1-thiol under severe conditions leads to the formation of a mixture of two regioisomeric sulfides (Scheme 56).

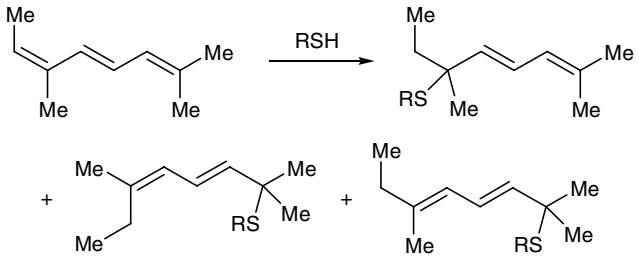
Scheme 56.



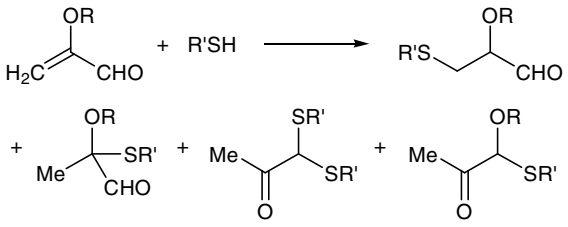
Mixtures of several products are usually formed by electrophilic addition of thiols to unsaturated compounds having two or more double bonds. An example is the addition of thiols to alloocimene in chloroform in the presence of $BF_3 \cdot Et_2O$, which gives a mixture of three sulfides [149] (Scheme 57). The number of final products may also increase due to isomerization or disproportionation of primary adducts, e.g., as it was

observed in reactions of thiols with 2-alkoxyprop-2-enals [150] (Scheme 58).

Scheme 57.



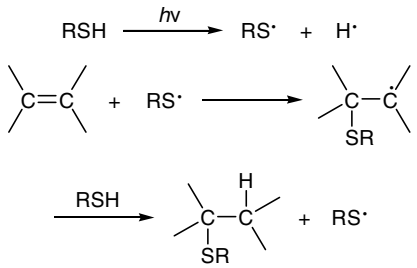
Scheme 58.



R = Et, Me; R' = Bu, CH_2=$CHCH_2$, Ph, $PhCH_2$.

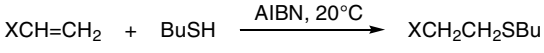
Radical addition of thiols at C=C bonds of unsaturated compounds is also well known. As a rule, it follows a radical chain mechanism and is initiated by UV irradiation or radical initiators [151] (Scheme 59).

Scheme 59.



Radical addition of thiols to olefins is usually characterized by a low energy of activation; therefore, such reactions require milder conditions, as compared to ionic addition, and in some cases are not accompanied by undesirable side processes. Thus ionic addition of thiols at the exocyclic C=C bond of 1-vinylpyrazole at 120°C gives a mixture of the corresponding α- and β-adducts, as well as of bis-sulfides $(RS)_2CHMe$ (R = Et, Bu, *i*-Bu) [152]; radical addition of butane-1-thiol at the C=C bonds of 1-vinylpyrazole and 1-vinylimidazole at 20°C [initiated by azobis(isobutyronitrile) (AIBN) or UV light] yields 9–52% of the corresponding β-adducts [152] (Scheme 60).

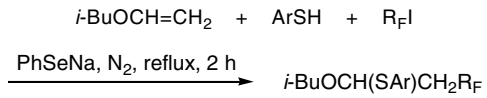
Scheme 60.



X = 1*H*-Pyrazol-1-yl, 1*H*-imidazol-1-yl.

Ultraviolet irradiation was used to initiate photochemical addition of ethanethiol and its derivatives to ethynyl(vinyl)silanes [153] and of 3-(diethoxyphosphoryl)propane-1-thiol to 1-allyloxy-2,3-epoxypropane [154]. Apart from AIBN [155], other chemical initiators are frequently used. Rodin et al. [156] described radical sulfanylation of 2-[2-(R-carbonyl)vinyl]furans with aliphatic thiols in the presence of *tert*-butyl peroxide [156], while radical perfluoroalkylarylsulfenylation of isobutyl vinyl ether was initiated by sodium benzeneselenolates [157]. In the latter case, a mixture of isobutyl vinyl ether, appropriate thiol, and perfluoroiodoalkane in anhydrous diethyl ether was heated in the presence of PhSeNa or 4-$MeOC_6H_4SeNa$ (Scheme 61).

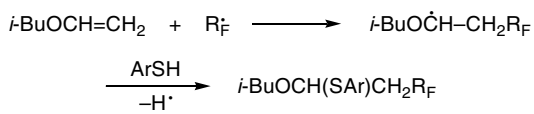
Scheme 61.



Ar = 4-$MeOC_6H_4$; $R_F = C_8F_{17}$.

The authors presumed [157] that one-electron transfer between the initiator and perfluoroiodoalkane gives rise to perfluorinated radical species $R_F^{\bullet}$ which adds at the double bond of vinyl ether (Scheme 62).

Scheme 62.

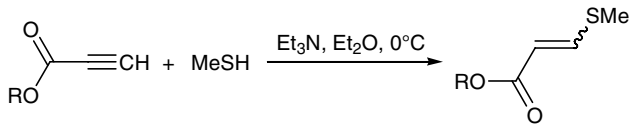


Oxidative addition of benzenethiol and 2-methylpropane-1-thiol to styrene was performed under conditions of phase-transfer catalysis in the presence of peroxo complexes of transition metals [158].

Addition of thiols at the triple C≡C bond in acetylenic compounds can also follow nucleophilic, electrophilic, and radical mechanisms. Nucleophilic addition implies the presence of base catalysts favoring formation of thiolate ions as reactive species. The addition of thiolate ion and the subsequent addition of proton may occur at both *trans* and *cis* position, depending on the nature of acetylenic substrate, thiol, solvent, and other factors. For example, nucleophilic addition of methanethiol at the C≡C bond of 2-meth-

oxybenzyl prop-2-ynoate gives a mixture of *Z* and *E* isomers of 2-methoxybenzyl 3-methylsulfanylprop-2-enoate at a ratio of 1:1.5 with an overall yield of 60% [159] (Scheme 63).

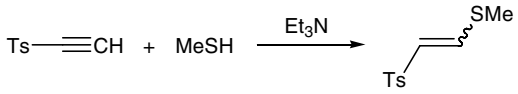
Scheme 63.



R = 2-$MeOC_6H_4CH_2$.

Likewise, mixtures of *Z* and *E* isomers are formed by nucleophilic addition of thiols at the triple bond of ethynyl *p*-tolyl sulfone [160] (Scheme 64).

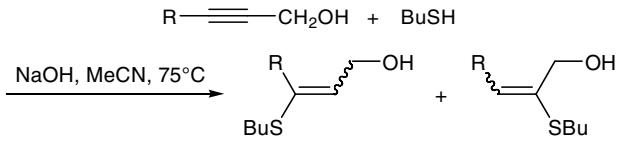
Scheme 64.



R = Et, Ph, 4-$MeOC_6H_4$, 4-$O_2NC_6H_4$.

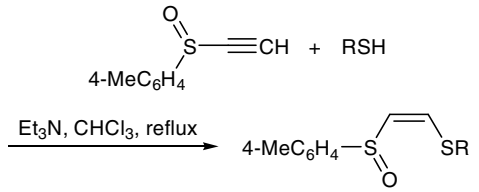
Disubstituted acetylenes could give rise to both stereo- and regioisomeric products, as in the nucleophilic addition of butane-1-thiol to 3-arylprop-2-yn-1-ols [161] (Scheme 65). The addition of thiols at the triple bond of ethynyl *p*-tolyl sulfoxide in chloroform in the presence of triethylamine was strictly stereoselective: only the corresponding *Z* isomers were obtained [162] (Scheme 66).

Scheme 65.



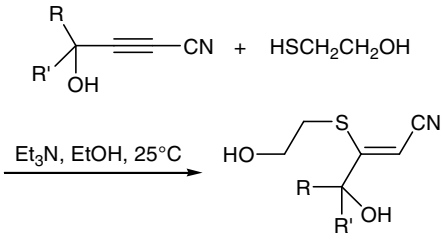
R = Ph, 4-NCC_6H_4.

Scheme 66.



Likewise, the corresponding *trans* isomers were formed by nucleophilic addition of 2-aminobenzenethiol to 1-benzoyl-2-trimethylsilylacetylene [163] and of imidazole-2-thiol to 3-phenylprop-2-ynenitrile [164]; in the two cases, the addition occurred exclusively at the sulfur atom. Skvortsov et al. [165] reported on quantitative *trans*-addition of 2-sulfanylethanol at the C≡C bond of tertiary β-cyano-α,β-acetylenic alcohols (Scheme 67).

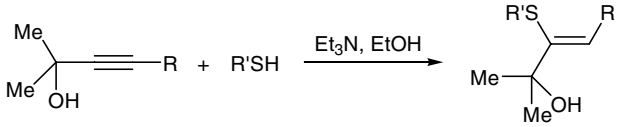
Scheme 67.



R = Me; R' = Me, Et; RR' = $(CH_2)_2$.

Quantitative and completely regio- and stereoselective nucleophilic *trans*-addition was observed in reactions of aliphatic and aromatic thiols with tertiary acetylenic alcohols having an ester [166] or cyano group [167] in the β-position with respect to the hydroxy group (Scheme 68).

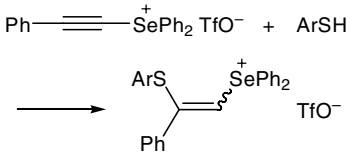
Scheme 68.



R = MeOCO, CN; R' = Alk, Ar.

2-Arylsulfanyl-2-phenylethenylselenonium salts were obtained by treatment of diphenyl(phenylethynyl)selenonium trifluoromethanesulfonate with arenethiols in isopropyl alcohol in the presence of triethylamine [168] (Scheme 69).

Scheme 69.

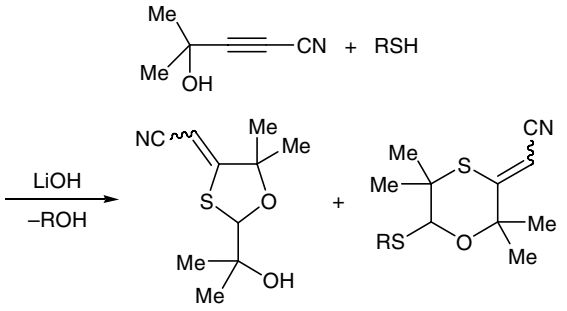


Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 2-HOC_6H_4.

Nucleophilic addition of quinolinethiols at the C≡C bond of tertiary cyanoacetylenic alcohols occurs in a very complex and nonselective fashion [169–171]. The product structure depends on the position of the SH group in the quinoline core. Quinoline-2-thiol reacts under relatively mild conditions to give a mixture of substituted 1,3-oxathiolane and 1,4-oxathiane (overall yield 72%) and quinolin-2-ol (up to 20%)

(Scheme 70). It was presumed [171] that these products result from transformations of primary adducts of quinoline-2-thiol at the triple C≡C bond.

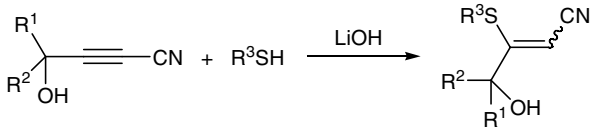
Scheme 70.



R = Quinolin-2-yl.

Unlike quinoline-2-thiol, quinoline-5-thiol reacted with tertiary cyanoacetylenic alcohols to afford 60% of 3-(quinolin-5-ylsulfanyl)prop-2-enenitrile [169, 170] (Scheme 71). The authors presumed formation of radical anions as reactive intermediates.

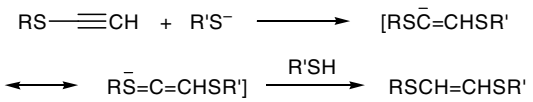
Scheme 71.



R^1 = Me; R^2 = Me, Et; R^1R^2 = $(CH_2)_3$; R^3 = quinolin-5-yl.

Nucleophilic addition of alkanethiols at C≡C bonds of alkylsulfanylacetylenes occurs very readily and quantitatively yields (*Z*)-1,2-bis(alkylsulfanyl)alkenes [172] (Scheme 72). The ease of the addition was rationalized [151] in terms of stabilization of the intermediate carbanion by *d* orbitals on the sulfur atom.

Scheme 72.

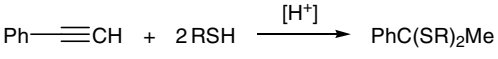


R = R' = Alk.

syn-Addition of thiols to acetylenes in the presence of Pd(II) and Rh(IV) complexes was reported to afford mainly the corresponding α-adducts [173].

Electrophilic addition of thiols to triple C≡C bonds is a very rare case. Probably, the only example of such reaction was described by Tokmurzin et al. [174] (Scheme 73). According to the authors, the process involves 2 equiv of thiol to give bis-sulfides.

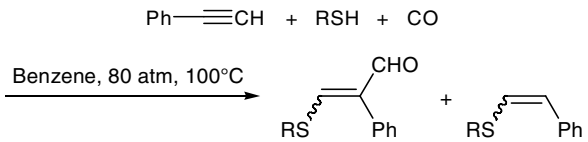
Scheme 73.



R = Pr, Bu.

Radical addition of thiols at C≡C bonds of acetylenic compounds was reported in a few publications. Sulfanyl radicals were generated by photochemical [151] and thermal methods [175], as well as using radical initiators [176, 177]. Conjugate addition of thiols and carbon(II) oxide to alkynes in the presence of AIBN gives mixtures of β-alkylsulfanyl-α,β-unsaturated aldehydes and the corresponding sulfides [176] (Scheme 74).

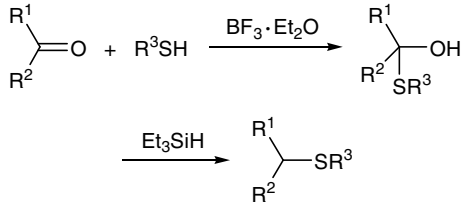
Scheme 74.



R = C_6H_{13}, C_8H_{17}, *t*-Bu, Ph.

Addition of thiols across the C=O bond of carbonyl compounds has been extensively studied; these reactions usually occur in the presence of acid catalysts. Depending on the reactant ratio and reaction conditions, two different products could be obtained. Reactions with equimolar amounts of the reactants lead to the formation of α-hydroxy sulfides which can readily be converted into other sulfides, including those having functional substituents. Olah et al. [178] described a one-pot synthesis of sulfides via addition of thiols at the C=O bond of carbonyl compounds, followed by reduction of α-hydroxy sulfides thus formed (Scheme 75).

Scheme 75.

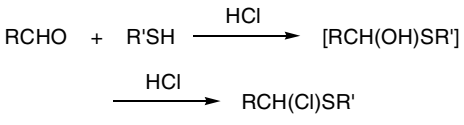


R^1 = H, Ph; R^2 = Ph; R^3 = *i*-Pr, *t*-Bu, Ph.

Thiols reacted with aldehydes in the presence of hydrogen chloride to give directly α-chloro sulfides [179] (Scheme 76).

An efficient procedure was developed for the introduction of phenylsulfanylmethylidene and phenyl-

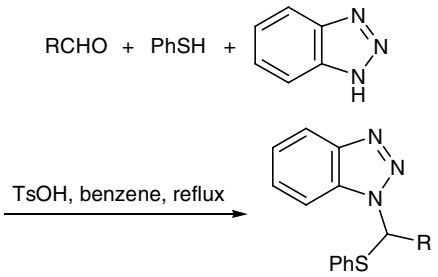
Scheme 76.



R = R' = Alk.

sulfanylmethyl groups into molecules of heterocyclic and natural compounds having labile hydrogen atoms. The procedure is based on the reaction of benzenethiol with aldehydes in the presence of proton donors. For instance, benzenethiol reacted with aldehydes in the presence of benzotriazole to produce 1-[α-(phenylsulfanyl)benzyl]-1*H*-benzotriazole [180] (Scheme 77).

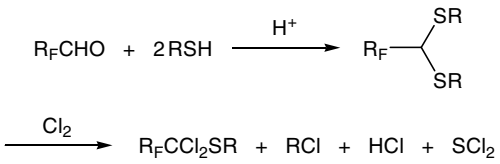
Scheme 77.



R = Ph, 4-MeC_6H_4.

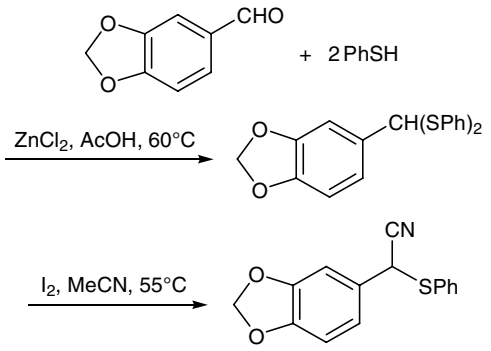
Likewise, using benzenethiol and formaldehyde, phenylsulfanylmethyl group was introduced into the 4-position of 3-oxo-13α,14β,17α-pregna-4,8-dien-20-yl acetate [181] and progesterone 20,20-ethylene acetal [182]. The use of excess thiol under acidic conditions favors transformation of carbonyl compounds into bis-sulfides or dithioacetals that are important intermediate products in the synthesis of various sulfur-containing compounds. Markovskii et al. [183] developed a procedure for the synthesis of α,α-dichloro sulfides via chlorination of dithioacetals derived from polyfluorinated aliphatic aldehydes (Scheme 78).

Scheme 78.



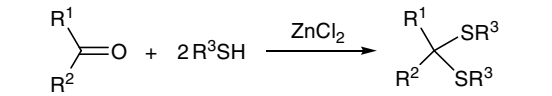
The reaction of piperonal with 2 equiv of benzenethiol in acetic acid in the presence of zinc(II) chloride gave the corresponding bis-sulfide, and treatment of the latter with iodine in acetonitrile afforded 3,4-methylenedioxyphenyl(phenylsulfanyl)acetonitrile [184]

Scheme 79.



(Scheme 79). A number of thioacetals were synthesized from ketones and thiols, and their reduction with PI_3 or P_2I_4 resulted in formation of mixtures of sulfides, hydrocarbons, and ketones [185] (Scheme 80).

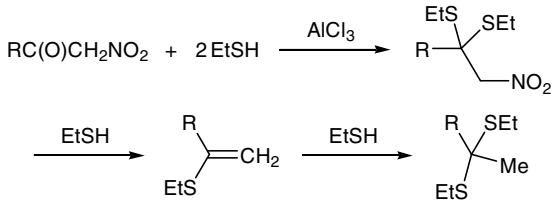
Scheme 80.



R^1 = Ph, 4-$MeOC_6H_4$; R^2 = Me, Ph; R^3 = Et, Ph.

The addition of ethanethiol at the carbonyl bond of α-nitro ketones in the presence of aluminum chloride or boron trifluoride–ether complex was accompanied by reductive substitution of the nitro group [186]. The process is likely to include initial formation of the corresponding dithioacetals, elimination of nitrous acid molecule to give ethyl alkenyl sulfides, and addition of the second thiol molecule at the double C=C bond (Scheme 81).

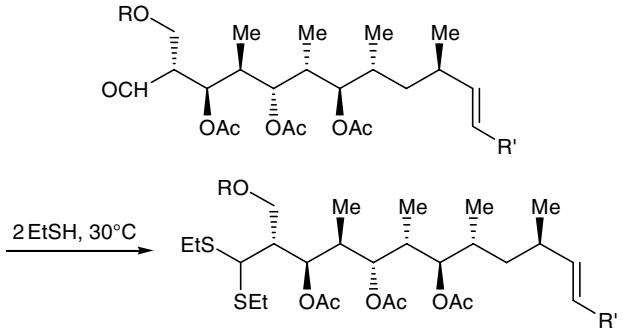
Scheme 81.



R = Me, Et.

In the recent years, thioacetalization of a carbonyl group with thiols has been widely used in syntheses and transformations of various natural compounds. Thioacetalization of appropriate aldehyde with ethanethiol in the presence of camphorsulfonic acid was the key stage in the total synthesis of antibiotic Rifamycin W [187] (Scheme 82).

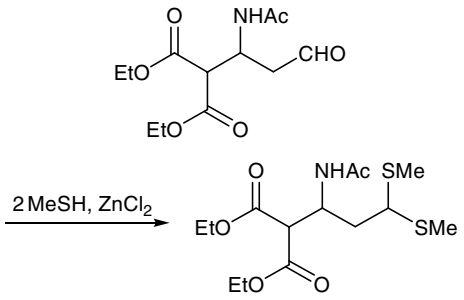
Scheme 82.



R = H, R' = COOMe.

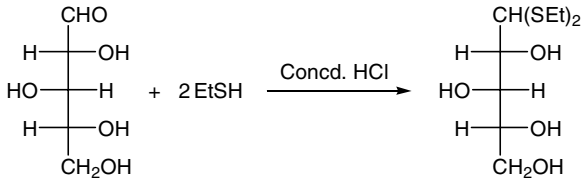
One step in the multistep synthesis of L-methionine was sulfanylation of the corresponding aldehyde with methanethiol using zinc(II) chloride as catalyst [188] (Scheme 83).

Scheme 83.



Thioacetalization of D-xylose with ethanethiol in the presence of concentrated hydrochloric acid was reported in [189] (Scheme 84).

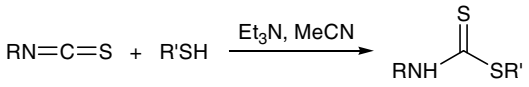
Scheme 84.



Concentrated hydrochloric acid was also used as catalyst in the synthesis of 4,5-di-*O*-acetyl-2,3-bis-(ethylsulfanyl)-D-lactose diethyl dithioacetal [190]. Trifluoroacetic acid [191] and boron trifluoride [192] were reported to catalyze thioacetalization of carbohydrates.

Studies on thiol addition at C=N bonds of isothiocyanates and Schiff bases and at C≡N bonds of nitriles are relatively few in number. It is known that reactions of alkanethiols with isothiocyanates lead to *S*-alkyl dithiocarbamates [193, 194] (Scheme 85).

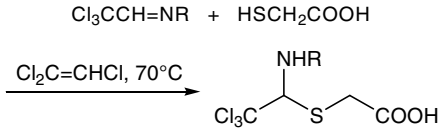
Scheme 85.



R = CH_2=$CHOCH_2CH_2$, $(CF_3)_2C$=C(Et); R' = Et, Pr, *i*-Pr, C_5H_{11}, C_6H_{13}, C_7H_{15}, $PhCH_2$.

Addition of thiols at C=N bonds of imines gives α-amino sulfides, as in the reaction of sulfanylacetic acid with *N*-substituted trichloroacetaldehyde imines [195] (Scheme 86).

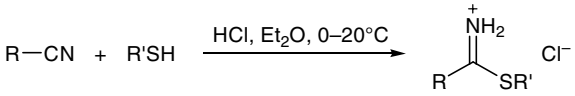
Scheme 86.



R = $PhSO_2$, 4-MeC_6H_4, 4-$MeOC_6H_4$.

Thiols react with nitriles in anhydrous medium in the presence of hydrogen chloride to give imidothioate hydrochlorides [196, 197] (Scheme 87).

Scheme 87.

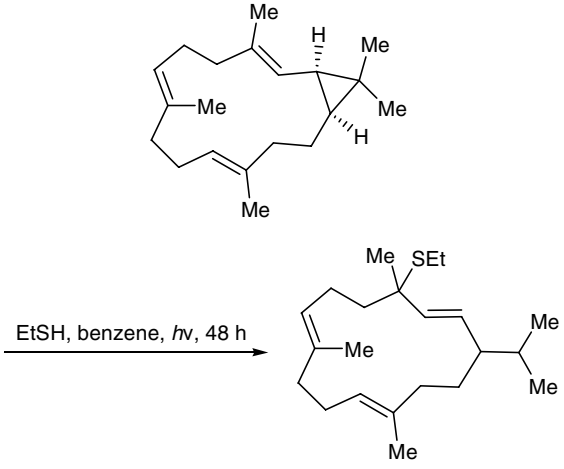


R = $NCCH_2$, indol-3-yl; R' = Bu, $PhCH_2$, Ph.

2.4. Ring Opening by the Action of Thiols

Opening of labile three-membered rings in cycloalkanes, oxiranes, thiiranes, and aziridines by the action of thiols is widely used for the synthesis of various functionalized sulfides. Pattenden and Smithies

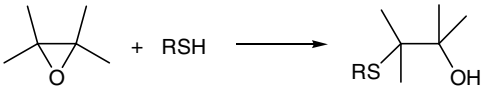
Scheme 88.



[198] described a radical stereocontrolled cleavage of the cyclopropane ring in a diterpene derivative by the action of ethanethiol under UV irradiation; the yield of corresponding sulfide was 75% (Scheme 88).

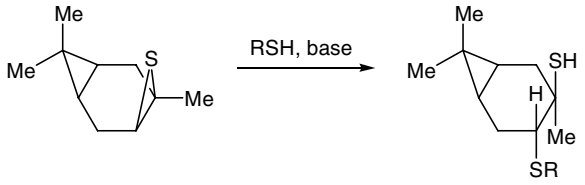
Opening of oxirane ring by the action of thiols underlies a preparative procedure for the synthesis of β-hydroxy sulfides [1] (Scheme 89) which are converted in some cases without isolation into the corresponding β-hydroxy sulfoxides [199]. Generally, the reaction is carried out by heating an epoxy derivative with thiol in an anhydrous inert organic solvent (benzene, toluene, etc.) [1, 200] or by treating the substrate with alkali metal thiolate in a polar solvent (dimethylformamide, tetrahydrofuran, etc.) [201–205].

Scheme 89.



The ring opening in mono- and disubstituted oxiranes by the action of triisopropylsilanethiol is completely regioselective, and the products are the corresponding 2-(triisopropylsiloxy)alkane-1-thiols [206]. Microwave-assisted reactions of 1-chloro-2,3-epoxypropane with thiols in dimethylformamide in the presence of a phase-transfer catalyst were reported to produce 80–90% of bis-sulfides $(RSCH_2)_2CHOH$ (R = Ph, 4-MeC_6H_4, $PhCH_2$, etc.) [207]. The thiirane ring in epithiacarane was cleaved by the action of thiols under basic conditions to obtain α-R-sulfanyl thiols [208] (Scheme 90).

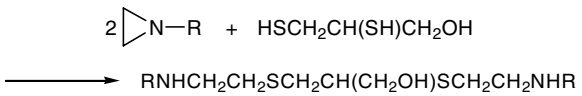
Scheme 90.



R = Me, Et, *i*-Pr, Bu, Ph.

Voronkov et al. [209] studied reactions of N-substituted aziridines with 2,3-bis(sulfanyl)propan-1-ol and obtained N,N'-substituted 4-hydroxymethyl-3,6-dithiaoctane-1,8-diamines (Scheme 91).

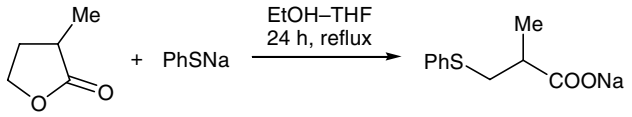
Scheme 91.



R = $PhCH_2CH_2$, $MeOCOCH_2CH_2$.

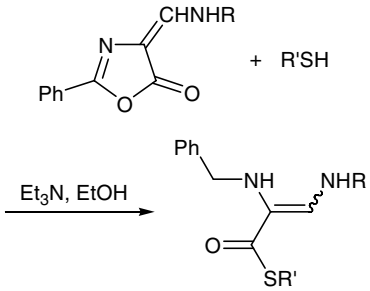
Opening of five- and six-membered rings in cyclic carbonyl compounds by the action of thiols was reported more rarely. The five-membered ring in α-methyl-γ-butyrolactone was cleaved by the action of sodium benzenethiolate to obtain sodium 2-methyl-4-phenylsulfanylbutanoate [210] (Scheme 92).

Scheme 92.



Opening of the five-membered ring in 4-(R-aminomethylidene)-2-phenyl-4,5-dihydrooxazol-5-ones on heating with thiols in the presence of triethylamine followed an analogous pattern [211] (Scheme 93).

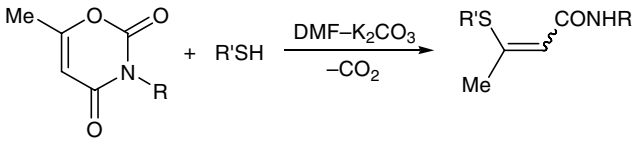
Scheme 93.



R = Ph, 4-MeC_6H_4; R' = Me, $PhCH_2$.

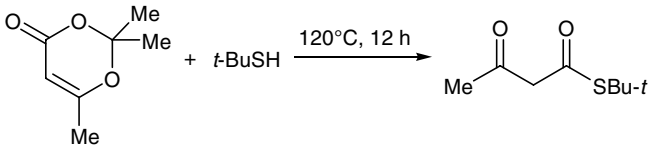
Kumar et al. [212] described reactions of thiols with 3-substituted 6-methyl-2,3-dihydro-4*H*-1,3-oxazine-2,4-diones; cleavage of the six-membered ring was accompanied by elimination of carbon dioxide, and mixtures of the corresponding *E*/*Z*-isomeric sulfides were formed (Scheme 94).

Scheme 94.



The reaction of 2-methylpropane-2-thiol with 2,2,4-trimethyl-4*H*-1,3-dioxin-4-one involves opening of the six-membered ring to give *S*-*tert*-butyl 3-oxobutanethioate as the major product [213] (Scheme 95). The authors believe [213] that the process is mediated by acetylketene which reacts with 2-methylpropane-2-thiol yielding the corresponding *S*-ester; [4+2]-cycloaddition of two acetylketene molecules gives rise to 3-acetyl-4-hydroxy-6-methyl-2*H*-pyran which was

Scheme 95.

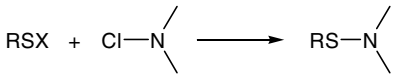


isolated as a by-product. Otani et al. [214] reported on the reaction of 3,4-di-*tert*-butyl-1-(4-tolylsulfonylimino-1λ^4-thiophene with sodium benzenethiolate in methanol; the authors succeeded in isolating and identifying disulfide PhSCH=C(*t*-Bu)C(*t*-Bu)=CHSSPh from the product mixture.

3. N-SULFANYLATION

Sulfanylation of *N*-halogenated compounds with thiols constitutes a preparative method for the synthesis of sulfenamides, both substituted and unsubstituted at the nitrogen atom [6] (Scheme 96).

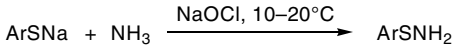
Scheme 96.



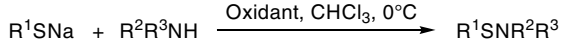
R = Alk, Ar, Ht; X = H, Na.

Various sulfenamides were synthesized by reactions of thiols with ammonia [215] and amines [216] in the presence of oxidants (Scheme 97).

Scheme 97.



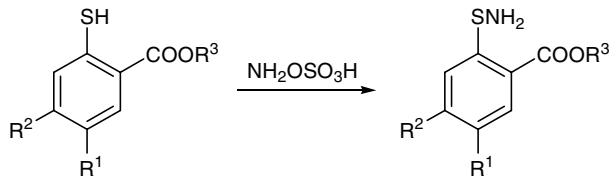
Ar = 2,4,6-$Cl_3C_6H_2$.



R^1 = Alk, Ar; R^2 = C_6H_{13}, R^3 = H; R^2R^3 = $CH_2CH_2OCH_2CH_2$.

Sulfenamides having no substituent on the nitrogen atom were obtained in 70–98% yield by reaction of thiols with hydroxylamine *O*-sulfonic acid in the presence of KOH [217] (Scheme 98).

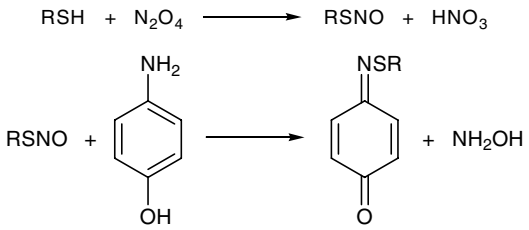
Scheme 98.



R^1 = H, Cl, MeO; R^2 = H, Cl, MeO; R^3 = Me, Et.

A two-step procedure was reported [7] for the synthesis of sulfenamides from thiols, *p*-aminophenol, and dinitrogen tetraoxide. In the first step, thiols reacted with N_2O_4 to form sulfenyl nitrites, and reactions of the latter with *p*-aminophenol gave the corresponding sulfenamides (Scheme 99).

Scheme 99.

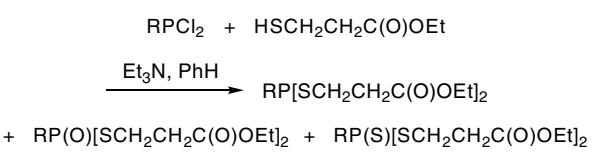


R = Alk, Ar.

4. P-SULFANYLATION

Nucleophilic substitution of chlorine at a phosphorus atom by RS groups is widely used in syntheses of various P,S-containing compounds. P-Sulfanylation is generally carried out in anhydrous solvents in the presence of bases (triethylamine, pyridine, etc.). These reactions are often accompanied by undesirable side processes. For example, the reaction of alkyl(aryl)dichlorophosphines with ethyl 3-sulfanylpropionate was accompanied by oxidation and sulfurization of the sulfanylation products [218] (Scheme 100).

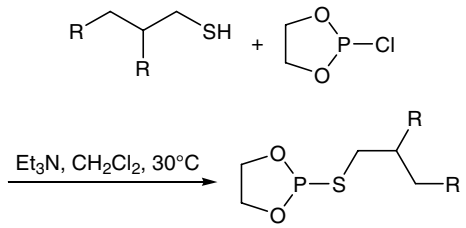
Scheme 100.



R = *t*-Bu, Ph.

To avoid side processes, P-sulfanylation is performed in an inert atmosphere. The reaction of 2-chloro-1,3-dioxaphospholane with 2,3-bis(stearoyloxy)-

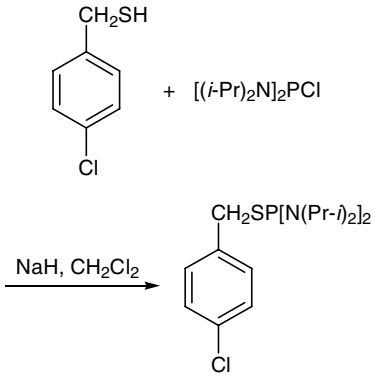
Scheme 101.



R = $C_{17}H_{35}C(O)O$.

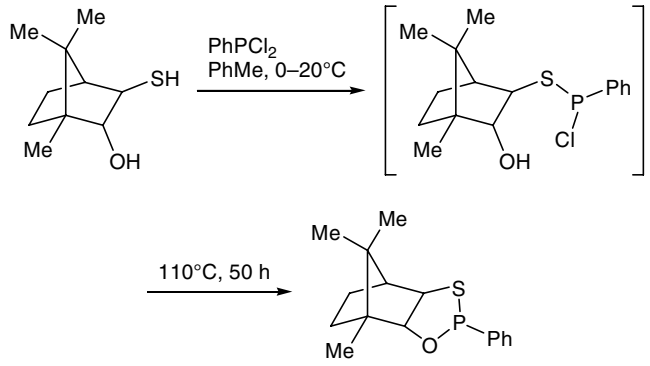
propane-1-thiol was carried out in anhydrous chloroform in the presence of triethylamine under argon [219] (Scheme 101). Chlorobis(diisopropylamino)phosphine was treated with *p*-chlorophenylmethanethiol in anhydrous methylene chloride using sodium hydride as a base [220] (Scheme 102).

Scheme 102.



Corey et al. [221] described sulfanylation of dichloro(phenyl)phosphine with bicyclic thiol, which was accompanied by intramolecular ring closure to give fused oxathiaphospholidine (Scheme 103).

Scheme 103.

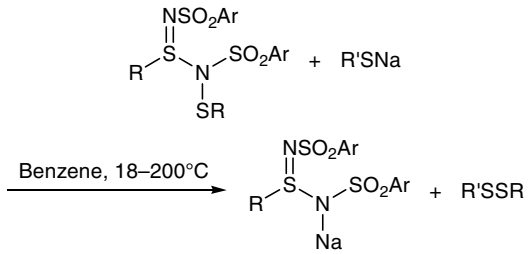


5. S-SULFANYLATION

Replacement of chlorine at the bivalent sulfur atom in sulfenyl chlorides by RS group is widely used for the synthesis of both symmetric and unsymmetric disulfides [222]. Apart from sulfenyl chlorides, other bivalent sulfur compounds such as sulfenyl thiocyanates [4], sulfenamides [6, 7], disulfides [223–225], thiosulfonates [226], and Bunte's salts [225] were recently involved in reactions with thiols to obtain unsymmetric disulfides. However, these procedures are still fairly rarely used, and the only preparative method for the synthesis of unsymmetric disulfides remains so far treatment of thiols with sulfenyl chlorides in the presence of organic bases.

Relatively recently, a new procedure has been proposed for the preparation of both symmetric and unsymmetric disulfides by reaction of sodium thiolates with *N*-arylsulfenyl-*N*,*N*′-bis(arylsulfonyl)arenesulfinimidamides in anhydrous benzene at room temperature [5] (Scheme 104).

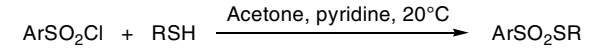
Scheme 104.



R = R' = Ph, 4-MeC_6H_4.

Replacement of chlorine at the S^{VI} atom in sulfonyl chlorides by RS group is not always selective. For example, heterocyclic thiols reacted with arenesulfonyl chlorides in acetone in the presence of pyridine to give the corresponding thiosulfonic acid *S*-esters [227] (Scheme 105).

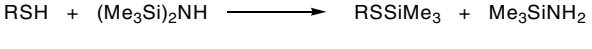
Scheme 105.



Ar = Ph, 4-MeC_6H_4, 4-$MeCONHC_6H_4$; R = 1*H*-benzimidazol-2-yl, 1-acetyl-1*H*-benzimidazol-2-yl.

On the other hand, reactions of 4-methylbenzenethiol with arenesulfonyl chlorides in the presence of triethylamine afforded triethylammonium sulfinates [228]. Medvedeva and Novokshonov [229] described silylation of thiols with hexamethyldisilazane; as a result, the corresponding trimethylsilyl sulfides were obtained (Scheme 106).

Scheme 106.

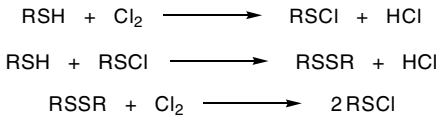


6. HALOGENOLYSIS OF S–H BOND AND FORMATION OF S-NITROSO DERIVATIVES

Halogenolysis of the S–H bond in thiols by the action of halogens is a preparative method for the synthesis of sulfenyl halides, which is widely used at present [230–232]. The chlorination is performed as a rule in anhydrous inert solvents (CCl_4, $CHCl_3$, etc.)

in the absence of UV light. The process includes three steps with participation of disulfides as intermediates (Scheme 107).

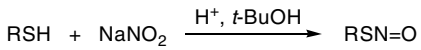
Scheme 107.



In the recent years, *N*-chlorosuccinimide (NCS) is frequently used as chlorinating agent [233–236]. An advantage of this reagent is high selectivity; reactions of thiols with NCS are not accompanied by chlorination of α-C–H bonds and other functional groups present in the substrate molecule. After separation of succinimide, the resulting sulfenyl chlorides can be brought into further transformations without isolation, which is very important in syntheses involving natural compounds. For instance, a solution of 4-chlorobenzenesulfenyl chloride prepared by chlorination of 4-chlorobenzenethiol with NCS in methylene chloride at 0°C was then used in the synthesis of thioether analogs of ergoline alkaloids [231]. Crombie et al. [234] described syntheses of rotenone analogs using a solution of benzenesulfenyl chloride in methylene chloride, which was prepared by treatment of benzenethiol with *N*-chlorosuccinimide at 0–2°C.

Reaction of thiols with precursors of nitrosyl cation lead to the formation of the corresponding S-nitroso compounds. The latter were formed, e.g., in reactions of thiols with sodium nitrite in *tert*-butyl alcohol in the presence of oxalic acid at 26–30°C [237] as shown in (Scheme 108).

Scheme 108.

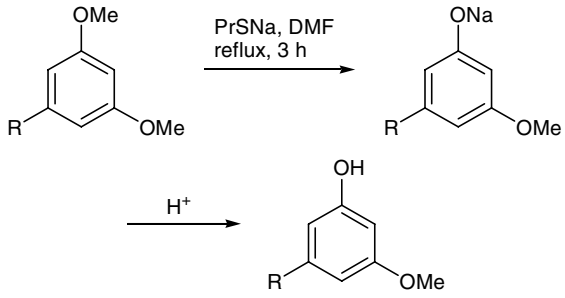


Some S-nitroso compounds were obtained by reaction of thiols with N_2O_4 in *tert*-butyl alcohol in the presence of 18-crown-6 [238]. Demir et al. [239] reported on the transformation of thiols into disulfides through S-nitroso intermediates.

7. DEALKYLATION WITH PARTICIPATION OF THIOLS

Thiolysis of C–O bonds by the action of thiols has been widely used to dealkylate alkyl aryl ethers. Two procedures for carrying out this reaction have been developed. The first of these implies heating of a mixture of an ether and sodium thiolate in a polar solvent (dimethylformamide, dimethyl sulfoxide, etc.). Following this procedure, selective demethylation of 1,3-dimethoxy-5-[(10*Z*)-pentadec-10-en-1-yl)benzene was performed [240] (Scheme 109).

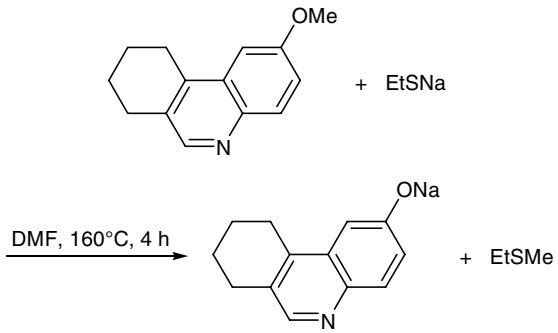
Scheme 109.



R = (10*Z*)-pentadec-10-en-1-yl.

Under analogous conditions, sodium ethanethiolate was used to effect demethylation of 2-methoxy-7,8,9,10-tetrahydrophenanthridine [241] (Scheme 110).

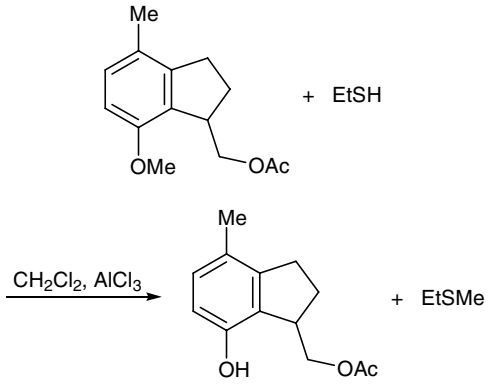
Scheme 110.



Bays et al. [242] utilized the same dealkylation procedure in the synthesis of a structural analog of morphine; in this case, lithium methanethiolate and sodium ethanethiolate were used as dealkylating agents.

The second procedure for dealkylation of alkyl aryl ethers is based on reactions of the latter with thiols in inert organic solvents in the presence of a catalyst ($AlCl_3$, $BF_3 \cdot Et_2O$, etc.). An example is demethylation of 1-acetoxymethyl-7-methoxy-4-methylindan [243] (Scheme 111). Some oxahydrindene derivatives were subjected to demethoxylation in the presence of boron trifluoride–ether complex [244]. However, this dealkylation procedure is not always effective. Furuta and Yamamoto failed to demethylate steroid ether using ethanethiol in the presence of $AlCl_3$ or ethane-1,2-dithiol in the presence of $BF_3 \cdot Et_2O$ [245].

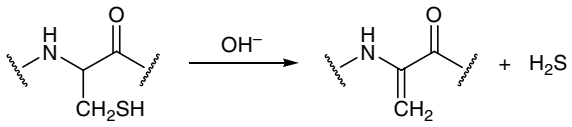
Scheme 111.



8. REACTIONS OF THIOLS INVOLVING CLEAVAGE OF THE C–S BOND

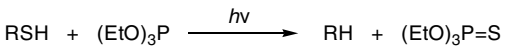
Reactions of this sort are few in number; however, some of these are very important from the practical viewpoint, e.g., for purification of oil from sulfur compounds. First of all, they include desulfurization of thiols which leads to unsaturated or saturated compounds, depending on the conditions. For example, treatment of cysteine-containing proteins with alkali results in elimination of the thiol groups from the cysteine fragments which are thus converted into dehydroalanine moieties [9] (Scheme 112).

Scheme 112.



Reactions of alkanethiols with triethyl phosphite under UV irradiation give saturated hydrocarbons [9] (Scheme 113).

Scheme 113.



Desulfurization of thiols can also be effected with the aid of nickel and its compounds in MeOH–THF (3 : 1) [246] or metallic sodium in liquid ammonia [247]. These reactions also give saturated products.

1,2,4-Triazole was obtained by oxidative desulfurization of 1,2,4-triazole-3-thiol with nitric acid [9]. Thermally induced intermolecular condensation of thiols with formation of sulfides is accompanied by cleavage of the C–S bond in one thiol molecule [1].

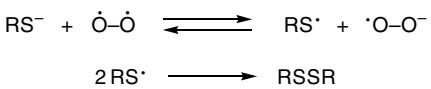
9. TRANSFORMATIONS OF THIOLS BY THE ACTION OF OXIDANTS

Oxidation of thiols with various oxidants gives the corresponding disulfides as primary products; the latter could then be oxidized to sulfenic, sulfinic, and sulfonic acids, depending on the oxidant nature and reaction conditions. Atmospheric oxygen is the most widely used oxidant both in the presence and in the absence of catalysts (Scheme 114).

Scheme 114.

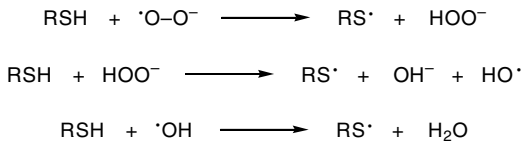
Noncatalytic oxidation is usually performed in alcoholic alkalies. It is believed that the oxidation process involves formation of sulfanyl radicals via one-electron transfer from thiolate ion to oxygen [151] (Scheme 115).

Scheme 115.



Peroxide radical anion thus formed also participates in the oxidation process (Scheme 116).

Scheme 116.

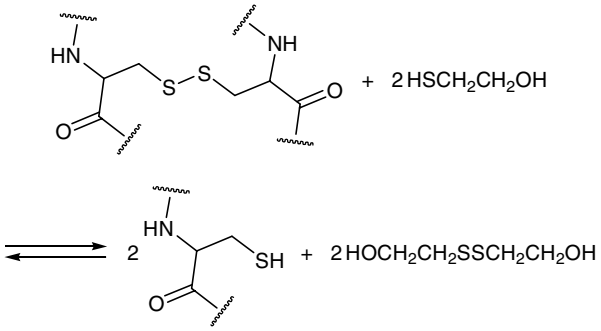


Apart from atmospheric oxygen, other oxidants and oxidizing systems are capable of effecting transformation of thiols into disulfides; the relevant data reported till 1997 inclusively were covered by review [248]. In the recent years, some less common oxidants and oxidizing systems have been proposed, e.g., silica-supported peroxosulfuric acid [249], sodium hypochlorite in acetonitrile [250], calcium hypochlorite in the presence of montmorillonite [251], carbon tetrabromide–potassium carbonate [252], phosphorus-containing chromium complexes in acetonitrile [253], crystalline ammonium peroxosulfate [254], moist HIO_3 [255], and vanadium oxide in combination with *tert*-butyl hydroperoxide [256]. Oxidations with atmospheric oxygen under microwave irradiation [257], hydrotalcite clay [258], and Fe(III)–NaI catalytic system [259] were also reported. Otaka et al. [260] successfully used

$Ti(OCOCF_3)_2$ to build up S–S bonds in the synthesis of cysteine-containing peptides. Various syntheses and transformations of natural compounds take advantage of reductive properties inherent to thiols; an example is reductive deiodination of 21-iodocorticosteroids [261].

While determining primary structure of cysteine-containing proteins, reductive cleavage of disulfide bridges is often necessary. This may be achieved, e.g., by treatment of proteins with excess ethanethiol or 2-sulfanylethanol [9] (Scheme 117).

Scheme 117.



Such reactions are referred to as intermolecular thiol–disulfide exchange, and they can be accelerated in the presence of such catalysts as guanidine hydrochloride [9] or selenium [262]. Among other oxidative transformations of thiols, oxidative imination with N-halogen and N,N-dihalogen derivatives must be noted. These reactions have been described in detail in recent reviews [263–266]; therefore, they are not considered in the present publication.

* * *

Various reactions of thiols described in the present review illustrate wide potential of these compounds in synthetic organic chemistry. Versatile reactivity of thiols originates primarily from their specific structure, namely from the presence of a highly reactive center, sulfur atom that can change its valence state, and high lability of the S–H bond which is capable of undergoing heterolytic or homolytic dissociation to give such reactive intermediates as sulfanyl radicals and S-centered cations or anions, depending on the conditions. Therefore, thiols have found wide application in fine organic synthesis for building up new S–C, S–N, S–P, S–S, S=O, S=N, and other bonds, and further studies on the reactivity of thiols will develop just in these lines.

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