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Synthesis and application of sulfenamides

I V Koval'

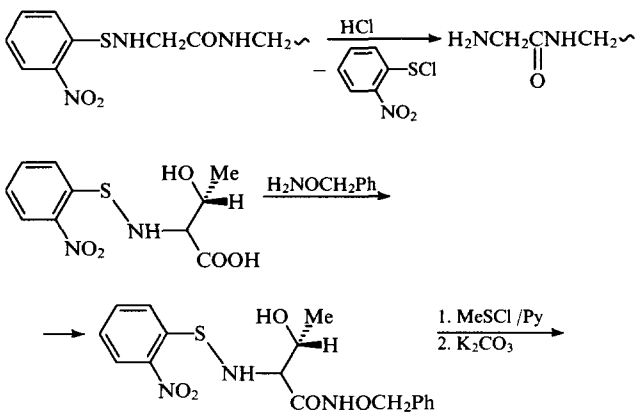
Contents

I. Introduction	421
II. Methods of sulfenylamide synthesis	422
III. The application of sulfenamides in organic synthesis	427
IV. Practical application of sulfenamides	435

Abstract. The results of studies on the use of sulfenamides in organic synthesis are systematised and generalised. The fields of industrial application of sulfenamides are considered. The bibliography includes 220 references.

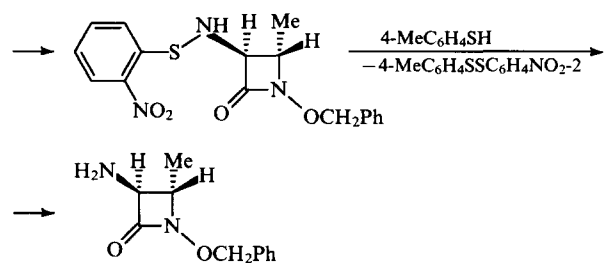
I. Introduction

The wide application of sulfenamides in fine organic synthesis is due to the specific features of their structure and reactivity, namely, to the existence of two active reaction centres (S and N), one of them having variable valence, and to the instability of the S – N bond which can rather readily be cleaved by both nucleophiles and electrophiles. High lability of this bond allows one to remove the sulfenyl moiety of the sulfenamide function, which is frequently used as a protective group in peptide synthesis,[1,2] and in natural product syntheses,[3,4] at a certain stage of synthesis. Elimination of the sulfenyl moiety occurs under sufficiently mild conditions by hydrochlorolysis or thiolysis of the S – N bond.

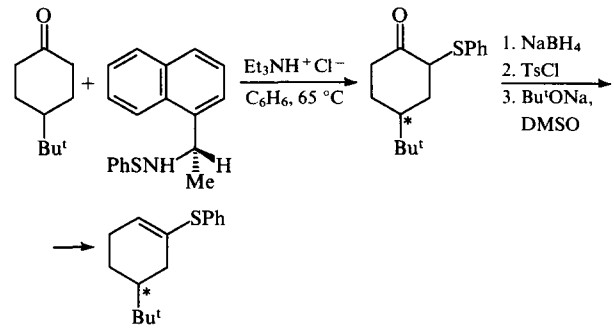


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On the other hand, the high lability of the S – N bond enables the sulfenamide function to be used for the introduction of a sulfenyl fragment into organic compounds under relatively mild conditions in multistep organic syntheses. Thus, the sulfenylation of 4-*tert*-butylcyclohexanone with chiral *N*-phenylthio-α-naphthylethylamine gives 62% of a diastereomeric mixture of the corresponding sulfides.[5] The reduction of this mixture with $NaBH_4$, subsequent tosylation and elimination of toluene-*p*-sulfonic acid gives a mixture of unsaturated sulfides with an isomer of *S*-configuration being predominant.



Yet another specific feature of sulfenamides is their tendency to generate both relatively stable and highly reactive intermediates (aminyl and sulfenyl radicals, radical cations, nitrenes, etc.) that participate in the transfer of sulfenyl and aminyl groups and in some other processes. The ability of the sulfur atom in sulfenamides to pass relatively readily from one valence state to another, as well as to increase its electron density at the expense of its shift from the adjacent *N*-anionic centre, is often used for the synthesis of compounds possessing four- and six-valent sulfur, for example, sulfur-containing imino compounds.

Bifunctional sulfenamides, i.e., sulfenamides containing both sulfenamide and other functional groups (Cl, Br, CCl_3, CF_2Cl, etc.) are synthetically very important. Based on such

sulfenamides, many preparative methods for the synthesis of various sulfur and nitrogen-containing heterocyclic compounds have been developed.

The primary products of sulfenamide transformations, such as aminosulfonium, thioammonium and sodium salts, are also widely used in organic synthesis, and numerous synthetic routes involve the conversion of sulfenamides to these products with their subsequent transformation without isolation from the reaction mixture.

In addition to fine organic synthesis, some sulfenamides are widely used in polymer chemistry, in agriculture, in the rubber industry, etc. These aspects are also considered in the present review.

II. Methods of sulfenylamide synthesis

1. Syntheses based on elemental sulfur

Elemental sulfur is not often used directly in the synthesis of sulfenamides because it has to be preactivated,[6] or highly reactive reagents have to be used. Probably only one example of the direct use of sulfur in sulfenamide synthesis, involving the interaction of elemental sulfur with various nitrobenzenes in liquid ammonia, has been described.[7] The reaction is accompanied by formation of the corresponding disulfides and sulfides, which is a drawback of the method.

2. Syntheses based on sulfenyl chlorides

The use of sulfenyl chlorides in the synthesis of sulfenamides is based on three main reactions:

(a) the sulfenylation of compounds containing N–H or N–X bonds (X = Li, Na, K, Ag, Me_3Si);

(b) the sulfenylation of inorganic isocyanates and the subsequent interaction of sulfenyl isocyanates with amines and alcohols;

(c) the addition of sulfenyl chlorides to the C=N or C≡N bond.

Based on these reactions, various preparative methods of sulfenamide synthesis have been developed. They are described in the published reviews,[8,9] and in the references cited in them. Later publications [10–21] are mostly devoted to the perfection of these methods and to the expansion of the scope of their application.

3. Syntheses based on thiols

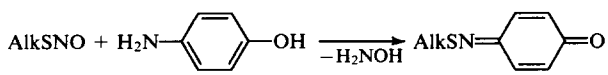
Amination of thiols with *N*-halo compounds, amines in the presence of oxidising reagents, sodium hydroxylaminosulfonate, and with other iminating reagents is the basis for a series of preparative methods of synthesis of unsubstituted and *N*-substituted sulfenamides (see review [22] and the references cited therein). The amination of thiols can also be performed using azides [23] in the presence of cuprous salts. The formation of disulfides and amines as side products is a drawback of the method.

$$R^1SH \xrightarrow{Cu^+} R^1SCu \xrightarrow{R^2N_3} R^1SNHR^2 + R^1SSR^1 + R^2NH_2$$

R^1 = Bu, Bz; R^2 = BuCO, HCO

A two-step synthesis of sulfenamides from thiols, *p*-aminophenol, and nitrogen dioxide has been described.[24] The first step involves the interaction of thiols with N_2O_4 to yield alkylsulfenyl nitrenes which then react with *p*-aminophenol (the second step).

$$AlkSH + N_2O_4 \xrightarrow[-HNO_3]{} AlkSNO$$



4. Syntheses based on disulfides

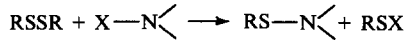
There are several methods of sulfenamide synthesis based on disulfides. One of them involves the interaction of disulfides with ammonia or amines in the presence of silver acetate or nitrate, or mercuric chloride in alkaline medium.[25,26]

$$R^1SSR^1 + 2R^2_2NH + MX \xrightarrow{NaOH} R^1SNR^2_2 + R^1SM + R^2_2NH\cdot HX$$

R^1 = Alk, Ar, Het; R^2 = H, Alk, Ar;
MX = $AgNO_3$, AgOAc, $HgCl_2$

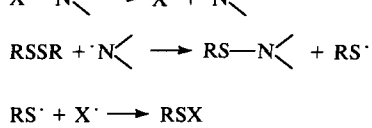
It is supposed [26] that a complex of disulfide with a metal is formed initially, which then undergoes nucleophilic attack by ammonia or amines to produce the sulfenamide and other products. The reaction is performed in methanol or ethyl acetate by treating equimolar amounts of disulfide and a metal salt with an excess of ammonia or the amine. The best yields of sulfenamides (60%–80%) were obtained with aromatic disulfides.

The second method of sulfenamide synthesis from disulfides is based on their reaction with *N*-halo compounds.



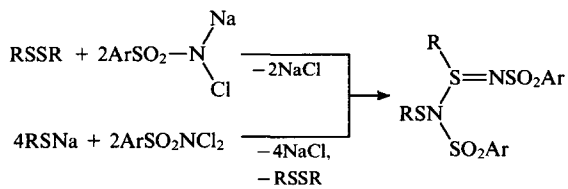
R = Alk, Ar; X = Cl, Br

The reaction occurs by a radical mechanism, which involves the homolysis of the N–X bond and the interaction of the N·-radical formed with the disulfide.

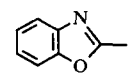


X = Cl, Br

To bind sulfenyl halides, pyridine, triethylamine, and other reagents are used. *N*-Chloro- and *N*-bromosuccinimide,[27] *N*-chlorophthalimide,[27] *N*-chloroformamidoyl chloride,[27] alkyl *N*-chlorobenzenecarboximidates, *N*-chloroimino-carbonates,[28] *N*-chlorobenzamide,[29] and *N*-chlorodialkylamines [30] react with disulfides according to this scheme. Sodium *N*-chlorosulfonamides react with disulfides in non-aqueous media to give sulfenamides of the general formula RSN(SO_2Ar)X [X = S(R)=NSO_2Ar][31] which can also be obtained by the reaction of sodium thiolates with dichlorosulfon-



R = Ph, 4-MeC_6H_4,



Ar = Ph, 4-MeC_6H_4

amides.[32]

The third method of sulfenamide synthesis from disulfides is their decomposition in the presence of lithium amides,[33] the yield of sulfenamides being as high as 62%–96%. As side products, Li thiolates are formed, which sometimes hinder the isolation of the target sulfenamides.

$$R^1SSR^1 + LiNR^2R^3 \longrightarrow R^1SNR^2R^3 + R^1SLi$$

R^1 = Pr^n, Ph; R^2 = H, Et, Pr^n, Pr^i, Bu^i;
R^3 = Et, Pr^n, Pr^i, Bu

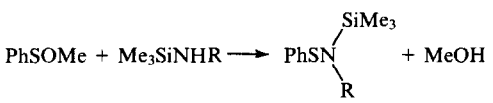
5. Syntheses based on arylsulfenates, sulfenyl thiocyanates, and thiolsulfonates

Sulfenamides are obtained in high yields by the sulfenylation of primary and secondary amines with esters of sulfenic acids.[23,34]

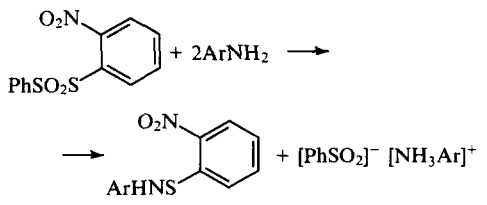
$$PhSOMe + HNR^1R^2 \longrightarrow PhSNR^1R^2 + MeOH$$

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

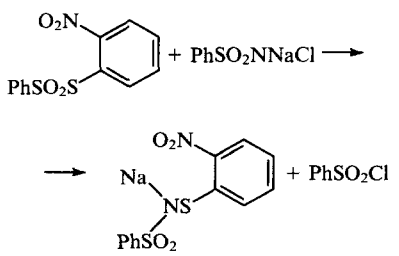
The use of sulfenates instead of sulfenyl chlorides as sulfenylation agents is sometimes preferable, in particular, if a substrate contains other highly reactive functional groups which are unstable toward sulfenyl chlorides. For example, trimethylsilyl derivatives of amines preserve the trimethylsilyl group upon interaction with sulfenates.[34]



The possibility of using thiolsulfonates for sulfenamide synthesis was first demonstrated by the sulfenylation of aromatic amines with *S*-(2-nitrophenyl) benzenethiosulfonate.[23,34] In this case the corresponding *N*-aryl-2-nitrobenzenesulfenamides were obtained in relatively good yields.



The reaction of *S*-(2-nitrophenyl) benzenethiosulfonate with sodium *N*-chlorobenzenesulfonamide to give *N*-(2-nitrophenylthio)benzenesulfonamide has been described.[35]

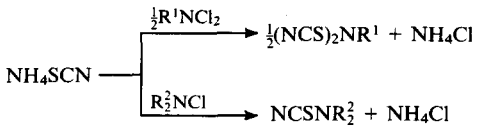


A series of *N*,*N*-dialkylsulfenamides have been obtained by the interaction of sulfenyl thiocyanates with a twofold excess of dialkylamine in ether.[36]

$$R^1SSCN + 2R^2_2NH \longrightarrow R^1SNR^2_2 + R^2_2NH \cdot HSCN$$

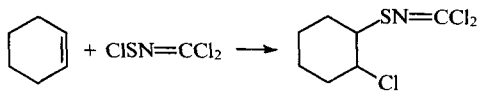
R^1 = Ph, Et, Pr, Bu; R^2 = Et, Bu^t

The possibility of using inorganic thiocyanates for the synthesis of sulfenamides has been demonstrated.[37] In particular, ammonium thiocyanate gives the corresponding sulfenamides on treatment with alkyl- and dialkylchloroamines.

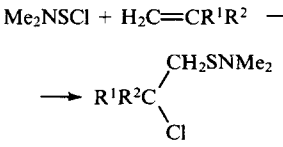


6. Syntheses based on *N*-chlorothio-compounds

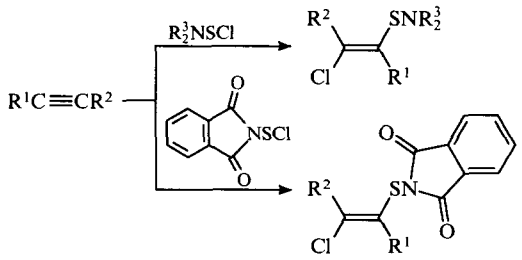
Two main routes of sulfenamide synthesis based on *N*-chlorothio-compounds have been developed. The first one involves the addition of *N*-chlorothio-compounds to C=C and C≡C multiple bonds. For example, *N*-(chlorothio)dichloroketimine adds to the C=C bond of cyclohexene to give 80% of the corresponding sulfenamide.[38]



The addition of *N*-(chlorothio)dimethylamine to unsymmetrical alkenes in the presence of iodine was shown[39] to be anti-Markovnikov with subsequent isomerisation of the adducts formed to more stable sulfenamides.



A series of *N*,*N*-disubstituted vinylsulfenamides was obtained by the addition of *N*-(chlorothio)dialkylamines[40] and *N*-(chlorothio)phthalimide[41-43] at the C≡C bond of alkynes.



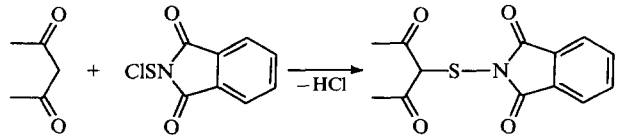
R^1 = Me, Et, Bu^t, Ph; R^2 = H, Me, Ph; R^3 = Me, Et

The second method of sulfenamide synthesis based on *N*-chlorothio-compounds is the treatment of CH-acids or their salts with *N*-chlorothio-compounds. For example, a series of *N*,*N*-(dialkyl)phenylacetylenesulfenamides has been synthesised by the interaction of *N*-(chlorothio)dialkylamines with lithium phenylacetylide.[40]

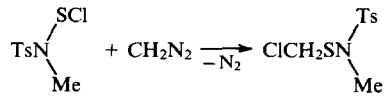
$$R_2NSCl + PhC{\equiv}CLi \xrightarrow[-LiCl]{} PhC{\equiv}CSNR_2$$

R = Me, Et

In the reaction of *N*-(chlorothio)phthalimide with dicarbonyl compounds containing activated C–H bonds sulfenamides are formed relatively readily and in high yields.[44,45]



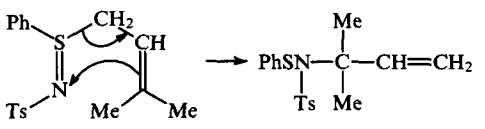
The synthesis of *N*-methyl-*N*-tosylchloromethanesulfenamide from *N*-(chlorothio)methyltosylamine and diazomethane has been reported.[38]



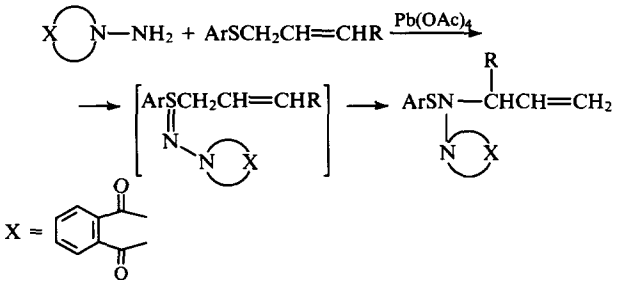
7. Syntheses based on sulfur imino compounds

a. Syntheses based on sulfynimines

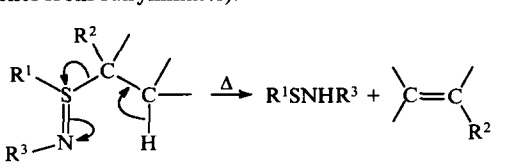
The ability of the S^{IV} atom in sulfynimines to undergo rather easy conversion to the bivalent state can be used in the syntheses of sulfenamides. Several synthetic routes have been developed depending on the structure of the initial sulfynimines. One of them is based on the [2,3]-sigmatropic rearrangement of *S*-allylsulfynimines, which involves migration of the allyl group from the sulfur to the nitrogen atom to produce the *N*-substituted sulfenamides.[32,46]



The tendency of *S*-allylsulfynimines to rearrange into more stable *N*-substituted sulfenamides is so pronounced that sometimes they cannot be isolated. For example, the reaction of nitrenes, obtained on treatment of *N*-amino-compounds with lead tetraacetate, with allyl aryl sulfides gave not *S*-allyl-*S*-arylsulfynimines, but the corresponding *N*-substituted sulfenamides.[47-50]



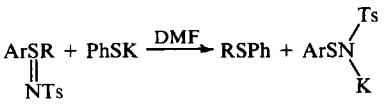
The second route for the synthesis of sulfenamides based on sulfynimines is the thermal rearrangement of *S*-alkylsulfynimines which contain a β-H-atom[46,51] (a thermal cycloelimination of alkenes from sulfynimines).



R^1 = Ar, Alk; R^2 = H, Me; R^3 = Ar, MeCO

The reaction occurs under relatively mild conditions and leads to sulfenamides in good yields. One shortcoming of this method is the possible formation of a mixture of two sulfenamides from sulfynimines containing two different alkyl groups at the sulfur atom, as, for example, in the thermolysis of *N*-tosyl-*S*-*tert*-butyl-*S*-isopropylsulfynimines.[52] *N*-Unsubstituted alkane- and arenesulfenamides,[52] as well as a series of *N*-substituted sulfenamides with aryl,[53,54] tosyl,[51] ethoxycarbonyl,[46] and carbamoyl[46] substituents were obtained by thermal cycloelimination of alkenes from sulfynimines.

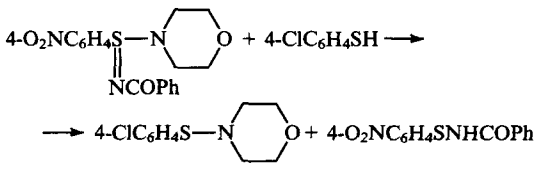
The third method of sulfenamide synthesis from sulfynimines is their reductive decomposition in the presence of thiolate anions. This reaction occurs on heating in DMF.[55]



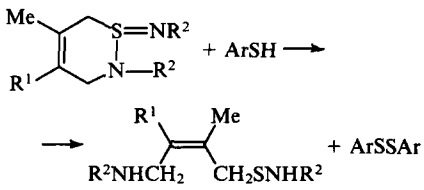
One drawback of this method is the formation of sulfides as side products, which complicates the isolation of the sulfenamides. On the other hand, an excess of thiolate can favour the decomposition of the sulfenamide formed.

b. Syntheses based on derivatives of sulfinimidic acids

Some amides of sulfinimidic acids undergo reductive cleavage in the presence of thiophenols to give sulfenamides. For example, the reductive cleavage of *p*-nitrobenzenesulfinimido amide in the presence of *p*-chlorothiophenol gives a mixture of two sulfenamides.[56]

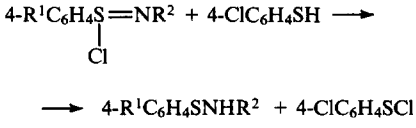


The reductive cleavage of imidodihydrothiazine, which can be considered as a cyclic amide of sulfinimidic acid, leads to aminobutenesulfenamides in 65%–95% yields.[57]



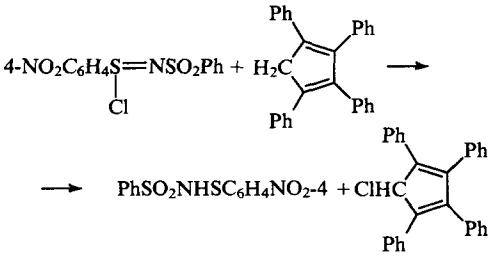
Ar = 4-ClC_6H_4, 4-MeC_6H_4

Sulfinimido chlorides react in a similar manner in the presence of thiophenols.[57]



R^1 = NO_2; R^2 = $PhSO_2$, PhCO

The reductive cleavage of sulfinimido chlorides to yield sulfenamides occurs also on treatment with some CH-acids.[58]

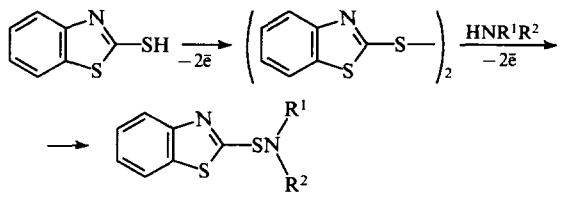




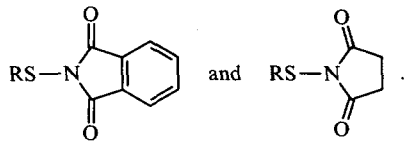
R^1 = Me, NO_2; R^2 = $PhSO_2$, PhCO, EtOCO

8. Electrochemical methods of synthesis of sulfenamides

N,N-Disubstituted benzothiazolesulfenamides were obtained by electrolysis of a 2-mercaptobenzothiazole–amine or bisbenzothiazol-2-yldisulfide–amine system in 70%–98% yield.[59]



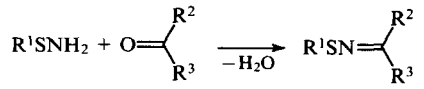
The electrolysis was performed with platinum electrodes in DMF in the presence of triethylammonium perchlorate. Under similar conditions, sulfenamides are formed from tetraalkylthiuramdisulfide, diphenyldisulfide, di-*tert*-butyl-disulfide, and dibenzyldisulfide.[60] The electrolysis of a disulfide–phthalimide and disulfide–succinimide system in the presence of NaBr in acetonitrile [60] gives the corresponding sulfenamides

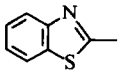


The mechanism of formation of these sulfenamides is believed [60] to involve a nucleophilic attack of the disulfide on the intermediate *N*-bromoimide.

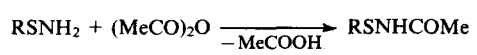
9. Modification of sulfenamides

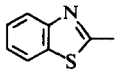
The change of sulfenamide structures by chemical modification of substituents at the sulfur and nitrogen atoms, as well as by the complete replacement of the amide or sulfenyl moieties, is the basis of methods for synthesising new types of sulfenamides. Chemical modification of the amide group of *N*-unsubstituted sulfenamides is the most common. The relatively high nucleophilicity of the nitrogen atom of the NH_2 group, as well as the availability of two active H atoms permit various chemical transformations. They are based on condensation with carbonyl compounds,[61–63] acylation,[23,64,65] sulfenylation,[8] phosphorylation,[23,66] etc.[34] Some examples of such reactions are given below.

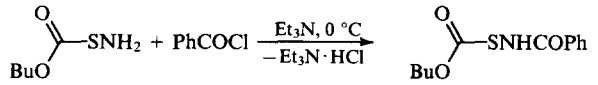


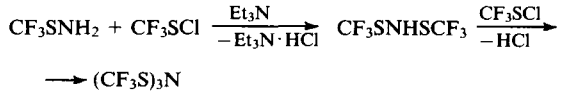
R^1 = CF_3, Ph, Ph_3C, PhCO, PhCS, ;

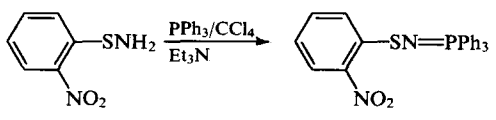
R^2 = Me, Et, Pr^i, Ph, $PhCH_2$; R^3 = H, Me, Et, Ph, $PhCH_2$



R = CCl_3CCl_2, 



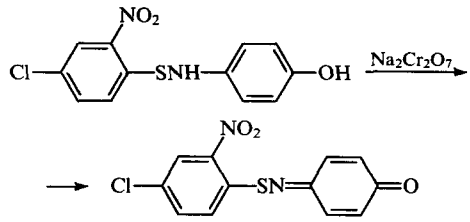




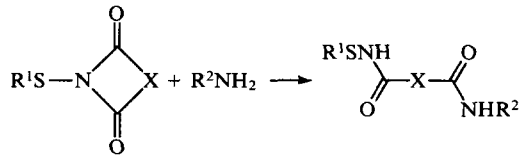
$ArSNH_2 + Ph_3PCl_2 \xrightarrow[-2Et_3N\cdot HCl]{2Et_3N} ArSN{=}PPh_3$

Ar = 4-$O_2NC_6H_4$, 2,4,6-$Cl_3C_6H_2$, C_6Cl_5

The modification of substituents at the nitrogen atom of sulfenamides,[34,67–70] or their complete substitution by other substituents [34,71–74] are also often used in the synthesis of new sulfenamides.



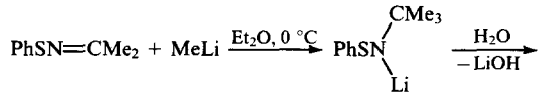
$ArSR + MeN{=}SO_2 \longrightarrow ArSN(Me)-SO_2R$

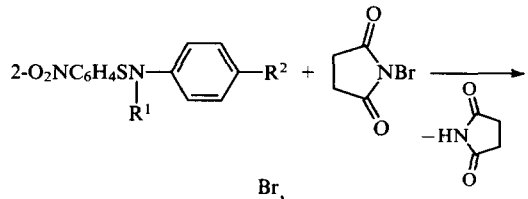


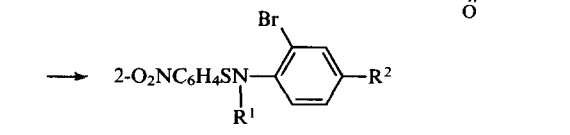
X = ; $-CH_2-CH_2-$

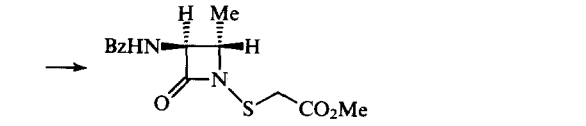
R^1 = Bu^t, Ph, cyclo-C_6H_{11}, n-C_8H_{17};

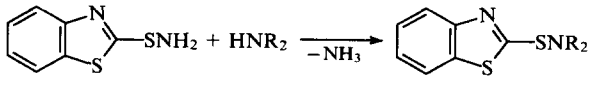
R^2 = Me, Pr^i, Bu, $PhCH_2$, n-$C_{18}H_{37}$



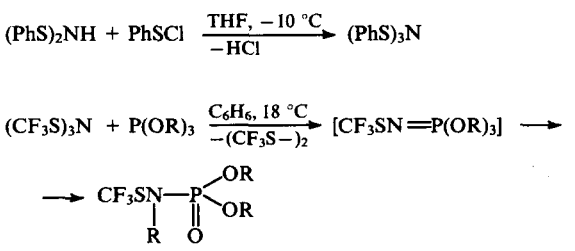




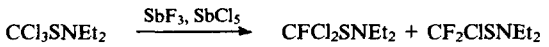




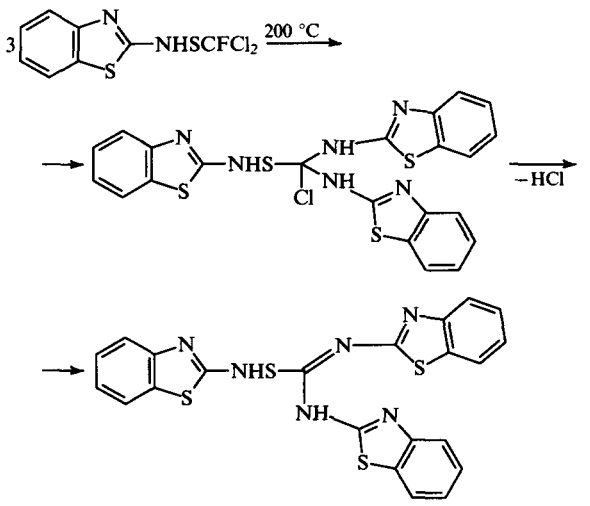
$PhSN(SiMe_3)_2 + R^1R^2C{=}O \longrightarrow PhSN{=}CR^1R^2$



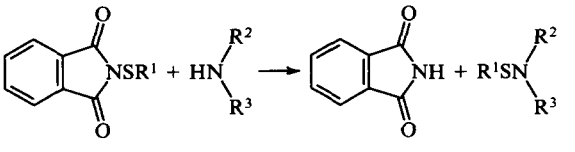
The chemical modification of radicals at the sulfur atom is not so frequently used for the synthesis of new sulfenamides. The substitution of one or two chlorine atoms by fluorine in *N,N*-(diethyl)trichloromethanesulfenamide using antimony trifluoride is an example of such modification.[8]



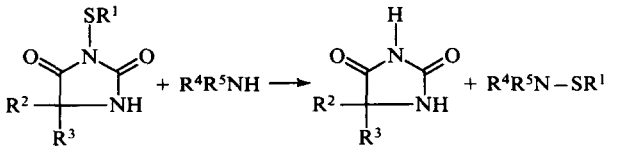
The thermolytic modification of the dichlorofluoromethyl group in *N*-(benzothiazole-2-yl)dichlorofluoromethanesulfenamide has been described.[38]



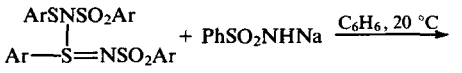
The complete substitution of the amide moiety can be performed on transamidation of sulfenamides in their interaction with *N*-nucleophiles whose nucleophilicity is higher than that of the amide moiety.[23, 32, 34]

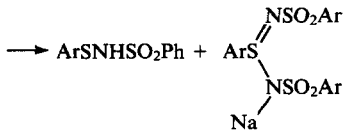


R^1 = Me, Et, Ph; R^2 = Me, Et; R^3 = Et, Pr^i



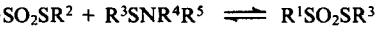
R^1 = CCl_3, Ph; R^2 = R^3 = Me; R^4 = H, Ph;
R^5 = $PhCH_2$; $R^4 + R^5 = -(CH_2)_3-$



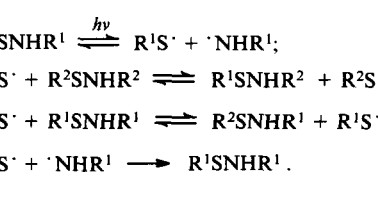


Ar = Ph, 4-MeC_6H_4

The replacement of the sulfenyl fragment in sulfenamides can result from the so called 'transsulfenylation', which involves the mutual exchange of sulfenyl groups between sulfenamides and other compounds containing these groups. For example, transsulfenylation of sulfenamides by esters of thiosulfonic acids has been described.[75]

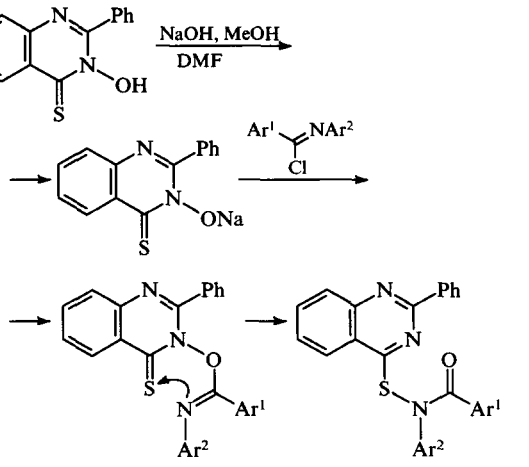


The mutual exchange of sulfenyl groups was observed upon photolysis of a mixture of two sulfenamides.[76] The photolysis is a radical process and involves the following transformations:

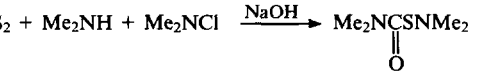


10. Other methods

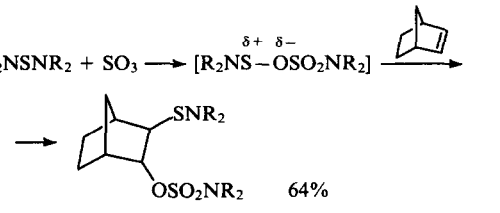
a. The sigmatropic rearrangement of the products of the reaction of 3-hydroxy-2-phenyl-4-thioxo-3,4-dihydroquinazoline with diarylimidoyl chlorides.[77]



b. The reaction of carbon disulfide with amines and *N*-chloroamines.[78]

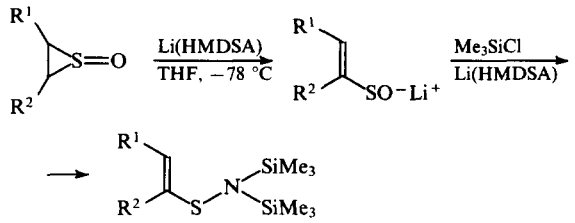


c. The addition of the products of sulfur trioxide insertion at the S–N bond of diaminosulfides to alkenes.[79]



R_2 = $-(CH_2)_5-$

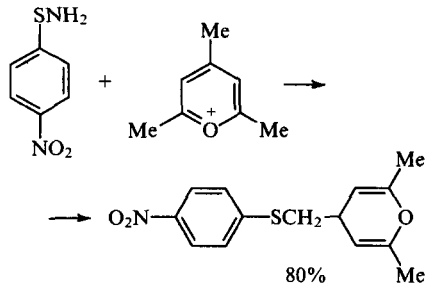
d. The interaction of alkylthiirane-*S*-oxides with lithium hexamethyldisilazide [Li(HMDSA)] and trimethylsilyl chloride.[80]



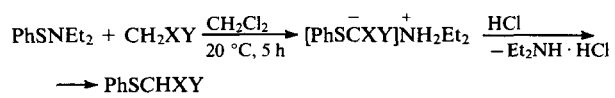
III. The application of sulfenamides in organic synthesis

1. Synthesis of sulfides

Several basic methods of synthesis of sulfides from sulfenamides have been developed. One of them is based on the sulfenylation of CH-acids or their salts with both substituted and *N*-unsubstituted sulfenamides. The sulfenamides are milder sulfenylating agents than sulfenyl halides; this fact allows their use in reactions with CH-acids which contain multiple bonds or functional groups which are vulnerable to sulfenyl halides. For example, the reaction of *p*-nitrobenzenesulfenamide with a 2,4,6-trimethylpyrilium salt produces the corresponding sulfide.[81]

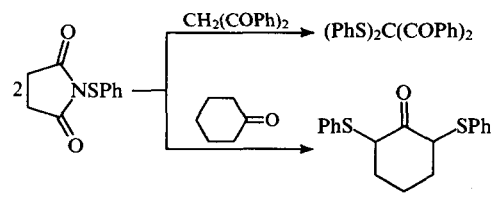


Sulfides are also obtained relatively smoothly and in good yields in the reaction of *N,N*-(dialkyl)arenesulfenamides with disubstituted methanes containing strong electron-withdrawing groups, such as CN, PhCO, MeCO, EtOCO, etc.[82]

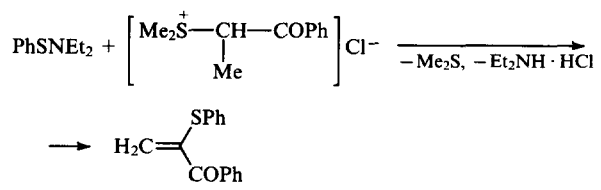


X	Y
CN	CN
PhCO	PhCO
MeCO	MeCO
MeCO	EtOCO
EtOCO	EtOCO

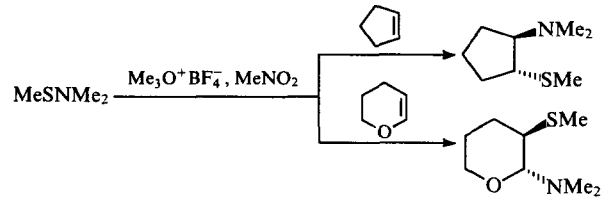
Excess of the sulfenamide can induce substitution of the second hydrogen atom of the CH-acid by the arylthio group.[23]



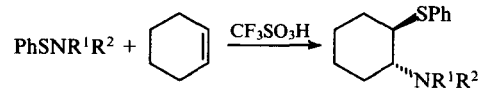
The synthesis of unsaturated sulfides by the sulfenylation of chlorosulfonium salts containing activated CH-bonds with sulfenamides has been described.[83]



The second method of sulfide synthesis from sulfenamides involves the addition of sulfenamides at the C=C bond of unsaturated compounds. This method is widely used for the synthesis of functionally substituted sulfides; several modifications of the method are known. The first one is the interaction of sulfenamides with alkenes in the presence of activating agents ($Me_3O^+BF_4^-$, $Et_2O \cdot BF_3$, CF_3SO_3H, etc.). The role of the activating agents is to increase the electrophilic properties of the sulfur atom in the initial sulfenamide, and to stabilise the intermediates formed. For example, the aminosulfenylation of cyclopentene and 3,4-dihydro-2*H*-pyran with *N,N*-(dimethyl)methanesulfenamide occurs rather smoothly in nitromethane in the presence of trimethyloxonium tetrafluoroborate.[84,85]

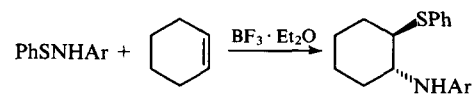


The addition of *N*-substituted benzenesulfenamides at the C=C bond of cyclohexene in the presence of trifluoromethanesulfonic acid has been described.[86]



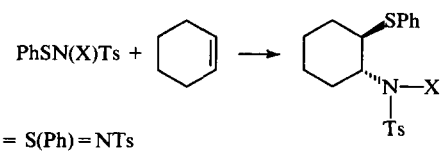
$R^1 = H$, $R^2 = Bu^t$; $R^1 + R^2 = -(CH_2)_5-$, $-(CH_2)_2O(CH_2)_2-$

Under analogous conditions, these sulfenamides add at the C=C bond of octene and indene.[86] *N*-(Aryl)benzenesulfenamides readily react with cyclohexene in the presence of boron trifluoride etherate to give the corresponding aminosulfides in 50%–90% yields.[87]



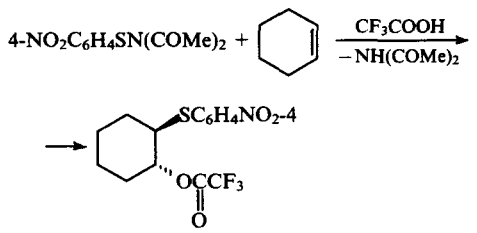
Ar = 4-$NO_2C_6H_4$, 4-ClC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$, 3-$MeOC_6H_4$

The sulfenamides PhSN(X)Ts [X = S(Ph)=NTs] add at the C=C bond of cyclohexene under acidic activation conditions to yield *N*-disubstituted aminosulfides.[88]

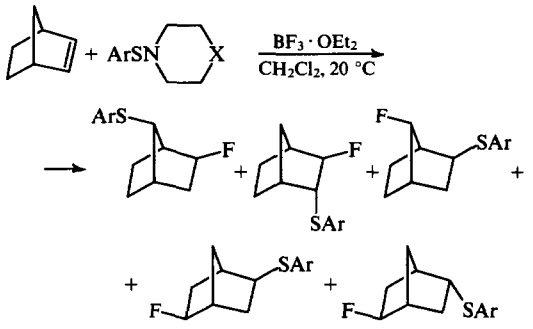


X = S(Ph)=NTs

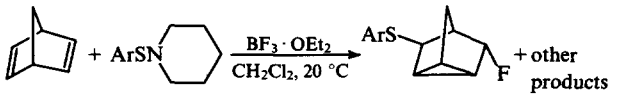
According to the second route, the participation of an external nucleophile in the reaction is envisaged, which provides a fragment substituting the amino group in the adduct. This route was first realised in the reaction of *N,N*-diacetyl-*p*-nitrobenzenesulfenamide with cyclohexene in the presence of trifluoroacetic acid.[88]



Apparently, in this case, an episulfonium intermediate is formed initially[84] in which ring-opening by trifluoroacetate anion leads to a *trans*-adduct. Thus, trifluoroacetic acid acts as both the activator and the external nucleophile. Likewise, boron trifluoride etherate has a double function in reactions of arenesulfenamides with norbornene[89] and norbornadiene.[90] The addition is accompanied by the rearrangement of the carbon skeleton resulting in a mixture of several products.

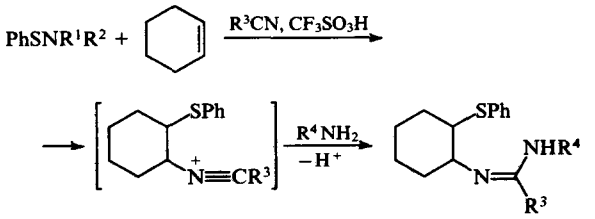


Ar = 2-$O_2NC_6H_4$; 2,4-$(O_2N)_2C_6H_3$; X = O, CH_2



Ar = 2,4-$(O_2N)_2C_6H_3$

Two reagents are generally used to accomplish the addition of sulfenamides to unsaturated compounds, one of them being an activator, and the other an external nucleophile. For example, the addition of *N*-substituted benzenesulfenamides to cyclohexene in the presence of trifluoromethanesulfonic acid and nitriles has been reported[91,92] to give sulfides with the amidine fragments. In this case, nitriles act as external nucleophiles.

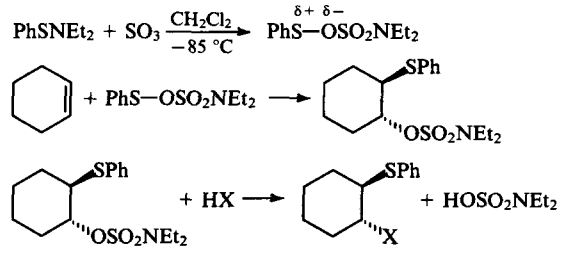


R^1 = R^2 = cyclo-C_6H_{11}; $R^1 + R^2 = -(CH_2)_2O(CH_2)_2-$;
R^1 = H, R^2 = Bu; R^3 = Me, Et; R^4 = Ph

The synthesis of sulfides of general formula $R^1HN.C(Me)=NC(R^2)=C(R^3)SPh$ with an acetamidine fragment (R^1 = Ph, 4-$O_2NC_6H_4$, 4-ClC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$; R^2 = H, Me, Et; R^3 = Me, Et, Pr, Bu) using the addition of *N*-(aryl)benzenesulfenamides to the corresponding alkynes in acetonitrile in the presence of boron trifluoride etherate has been described.[93]

The addition of *N*-(*p*-nitrophenyl)benzenesulfenamide to alkynes $R^1C{\equiv}CR^2$ (R^1 = H, R^2 = Me; R^1 = H, R^2 = Bu^t; R^1 = H, R^2 = Pr; R^1 = H, R^2 = Bu; R^1 = Me, R^2 = Pr; $R^1 = R^2$ = Me; $R^1 = R^2$ = Et; $R^1 = R^2$ = Pr; R^1 = H, R^2 = Ph; R^1 = Me, R^2 = Ph; R^1 = Et, R^2 = Ph; $R^1 = R^2$ = Ph) in acetic acid in the presence of boron trifluoride etherate is a stereospecific reaction, which results in a mixture of two products, (*E*)-$R^2C(OAc)=C(R^1)SPh$ and (*E*)-$R^1C(OAc)=C(R^2)SPh$, in total yields of 30% – 80%.[94,95]

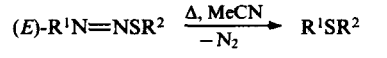
The third route to sulfides by the addition of sulfenamides at multiple bonds involves enhancement of the sulfur atom electrophilicity by insertion of sulfur trioxide into the S–N bond of sulfenamides with the subsequent addition of the insertion product to the C=C bond of alkenes (that is, sulfamatosulfenylation of alkenes).[96] For example, the addition of *N*,*N*-(diethyl)benzenesulfenamide to cyclohexene in the presence of sulfur trioxide in chloroform yields a *trans*-1,2-adduct, which is converted to the corresponding functionally substituted sulfide upon treatment with acid.[97]



X = Br, MeCOO, CF_3COO, HCOO

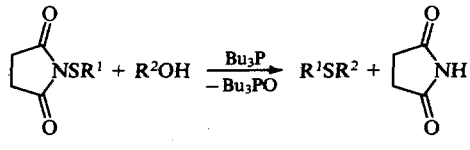
The sulfamatosulfenylation of norbornene and norbornadiene[98] is accompanied by rearrangement of the carbon skeleton and results in a mixture of different sulfides that are difficult to separate. The use of pyridine–sulfur trioxide as a donor of SO_3 allows one to perform the sulfamatosulfenylation of alkenes at ambient temperature.[99] The addition of sulfenamides to alkenes in the presence of sulfamic acid[100,101] and potassium persulfate[102] has also been studied.

Yet another method of sulfide synthesis from sulfenamides which should be mentioned involves thermal decomposition of arylthioazo compounds.[103]



R^1 = 4-NCC_6H_4, 4-$O_2NC_6H_4$; R^2 = Bu^t, Ph

The thermolysis is believed[103] to occur by aromatic nucleophilic substitution ($S_{RN}1$) through the intermediate radical anion $[R^1N=NSR^2]^{\cdot -}$. The formation of sulfides, together with other products, was observed[104] in the reaction of sulfenamides with alcohols in the presence of trialkylphosphites.



2. Synthesis of sulfenyl halides

The treatment of sulfenamides with hydrogen halides in anhydrous organic solvents yields the corresponding sulfenyl halides.



The reaction has preparative value, but it is not often used for the synthesis of sulfenyl halides, because the starting sulfenamides are usually synthesised from the same sulfenyl halides, to which they are then converted. The transformation of a sulfenyl halide function to sulfenamide followed by cleavage of the S–N bond with gaseous hydrogen halide is used as a synthetic method in the modification of a sulfenyl halide aimed at protecting the sulfenyl

halide function,[8] as well as in peptide synthesis, in which the sulfenyl fragment acts as a protective group. 2-Nitrobenzenesulfenyl chloride forms crystalline sulfenamide derivatives with amino acids, which can rather readily be cleaved in the presence of hydrogen chloride; this appeared to be of particular value in peptide synthesis.[105] The triphenylmethanesulfenyl group is also successfully used as a protective group in the synthesis of alkaloids.[34]

3. Synthesis of disulfides

Thermolysis, thiolysis, and hydrolysis of sulfenamides are the most common processes for the practical synthesis of disulfides among a wide range of reactions of sulfenamides that give disulfides. The homolytic cleavage of the S–N bond upon the heating of sulfenamides gives thiyl radicals which recombine to disulfides. The choice of thermolysis conditions depends both on the basicity and the structure of the initial sulfenamides. For example, the thermolysis of tri(phenylsulfenyl)amine occurs under rather mild conditions at ~50 °C to yield diphenyldisulfide.[106]

$$2(PhS)_3N \rightleftharpoons 2(PhS)_2N^{\cdot} + 2PhS^{\cdot}$$

$$2(PhS)_2N^{\cdot} \rightleftharpoons (PhS)_2N{-}N(SPh)_2$$

$$(PhS)_2N{-}N(SPh)_2 \longrightarrow PhSN{=}NSPh + 2PhS^{\cdot}$$

$$PhSN{=}NSPh \longrightarrow 2PhS^{\cdot} + N_2$$

$$2PhS^{\cdot} \longrightarrow PhSSPh$$

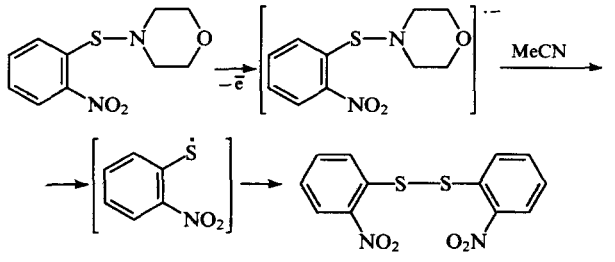
The thermolysis of *N*-(aryl)benzenesulfenamides requires more severe conditions, the products being diaryldisulfides and azobenzene.[107]

$$2PhNHSAr \xrightarrow{195\ ^{\circ}C} 2ArS^{\cdot} + 2\,PhNH^{\cdot}$$

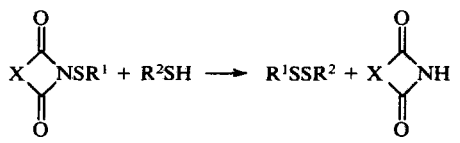
$$2ArS^{\cdot} \longrightarrow ArSSAr$$

$$2PhNH^{\cdot} \longrightarrow PhHN{-}NHPh \xrightarrow[-H_2]{} PhN{=}NPh$$

The homolytic cleavage of the S–N bond with the subsequent recombination of the thiyl radicals formed was observed during the anodic oxidation of *N*-(2-nitrophenylthio)morpholine in acetonitrile in the presence of NaClO.[108]

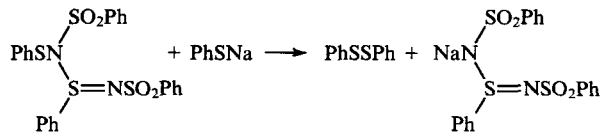


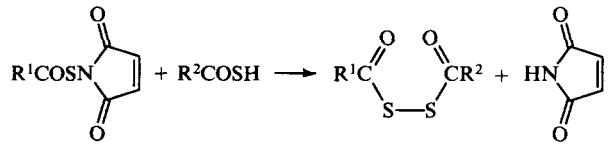
The thiolysis of sulfenamides is used in the synthesis of both symmetrical and unsymmetrical disulfides. Nucleophilic substitution of the amide group at the sulfur atom of sulfenamides by an alkyl- or arylthio group occurs upon their interaction with thiols[34,109] or thiolates,[110] thioacids,[111] alkyl- or arylthiosilanes.[112]



X = $-(CH_2)_2-$, $-CH{=}CH-$

$$ArSNHC_6H_4NO_2\text{-}4 + RSH \xrightarrow[-4\text{-}O_2NC_6H_4NH_2]{1.5\ \text{equiv. } BF_3} ArSSR$$

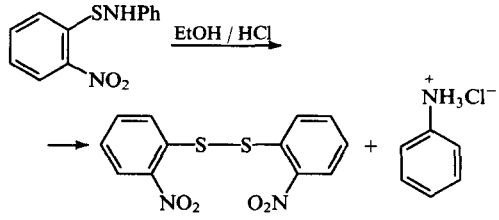




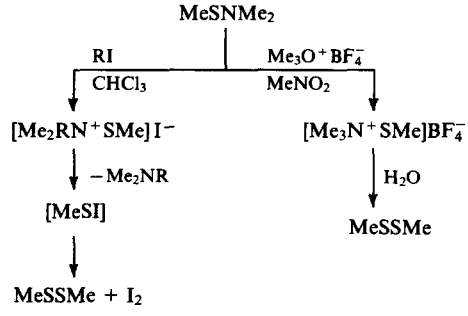
$$PhSNMe_2 + Me_3SiSR \longrightarrow PhSSR + Me_3SiNMe_2$$

However, the synthesis of unsymmetrical disulfides is accompanied by the formation of a small amount of symmetrical ones,[109] this being the drawback of the method.

The hydrolysis of sulfenamides in acid–alcoholic media results in the formation of symmetrical disulfides.[23] They are, apparently, disproportionation products of sulfenic acids that are formed at the first stage of the hydrolysis.

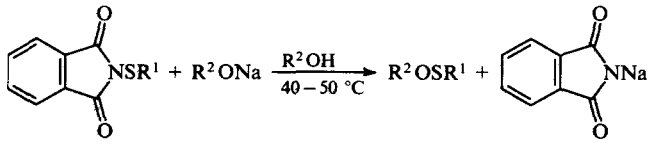


Symmetrical disulfides are also formed upon decomposition of thioammonium salts resulting from the alkylation of sulfenamides with alkyl halides or trialkyloxonium salts.[113]

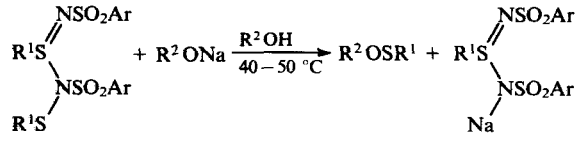


4. Synthesis of sulfenic esters

N,*N*-Disubstituted sulfenamides having strong electron withdrawing substituents relatively readily undergo alcoholysis in the presence of alkoxides. Alkyl sulfenates are produced in this way. For this purpose, *N*-(alkylthio)phthalimides[114,115] are most frequently used. They react with alkoxides in alcoholic media to form the corresponding sulfenates.



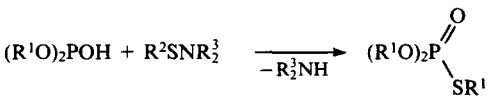
N-Arylsulfenyl-*N*,*N*′-bis(arylsulfonyl)arenesulfinamidines undergo even easier alcoholysis.[32,116,117]



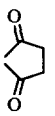
The use of sulfenamides for the synthesis of sulfenates is preferable to that of sulfenyl chlorides, because the latter often induces undesirable side processes.[104]

5. Synthesis of compounds with a P–S bond

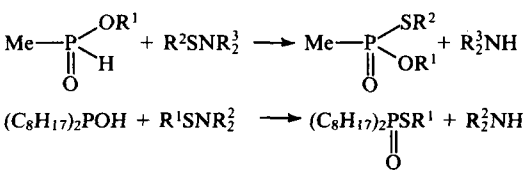
The use of sulfenamides for the synthesis of various phosphor–sulfur-containing compounds is based on phosphorolysis of the S–N bond with phosphorylating reagents. The synthesis of thiolphosphates using the interaction of *N,N*-disubstituted sulfenamides with dialkyl phosphites has been described.[118,119]



R^1 = Me: R^2 = Bu, Bu^t, R^3 = Me, Et; R^2 = Ph, R^3_2 =

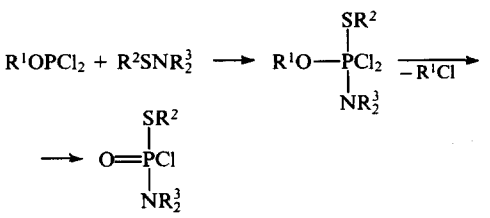


The syntheses of thiolphosphonates and thiolphosphinates were performed in a similar manner.[119]



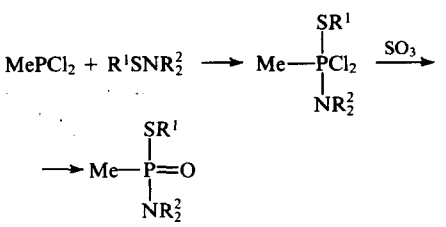
R^1 = Et, Pr, Bu; R^2 = Me, Bu; R^3 = Me, Et

The reaction of sulfenamides with alkyl phosphodichloridites yields alkyl (amido)thiophosphochloridates.[119]



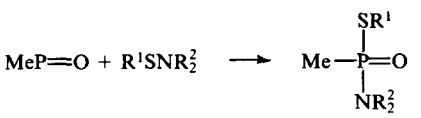
R^1 = Me; R^2 = Bu, Bu^t; R^3 = Me, Et

The reaction of sulfenamides with methyldichlorophosphine gives phosphoranes, which may be converted to *S*-alkyl dialkylamidothiophosphonates upon treatment with sulfur trioxide.[23]



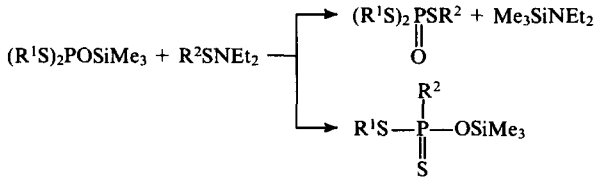
R^1 = Bu, Bu^t; R^2 = Me, Et

Similar compounds are formed when sulfenamides react with methylphosphonous anhydride.[23]



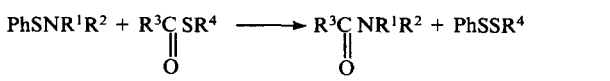
R^1 = Bu, Bu^t; R^2 = Me, Et

Sulfenamides react with *S,S*-dialkyl-*O*-trimethylsilyl dithiophosphites to yield trithiophosphates.[120] In this case, a part of the initial *O*-trimethylsilyl dithiophosphite is transformed to *S*-alkyl-*O*-trimethylsilyl dithiophosphonate.

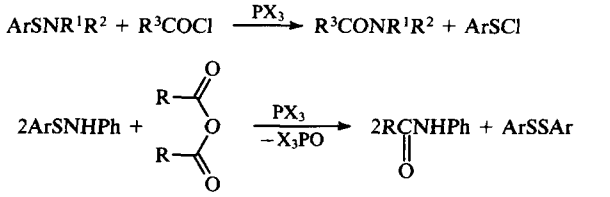


6. Synthesis of nitrogen-containing compounds

Sulfenamides are good amidating reagents with respect to *S*-esters of thiocarboxylic acids, carboxylic anhydrides, and acyl chlorides. This feature is often used in syntheses of various *N*-substituted carboxyamides. The corresponding reactions occur in the presence of tervalent phosphorus compounds under rather mild conditions to give the target products in high yields.[23,121–123]

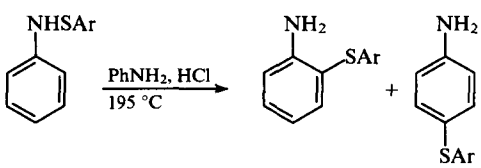


R^1 = Me, Et, Bu, Bz; R^2 = Me, Et, Bu, Pr^i;
R^3 = Me, Et, Bu, Ph; R^4 = Ph, 4-$O_2NC_6H_4$



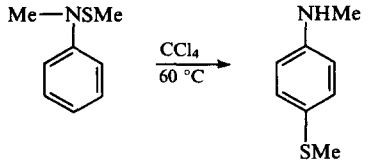
The role of the catalyst is to form the intermediate phosphonium salts with sulfenamides having a highly polarised S–N bond.[124]

Different rearrangements of sulfenamides are often used in the syntheses of functionally substituted aromatic amines. For example, the heating of *N*-(phenyl)arenesulfenamides in aniline in the presence of hydrochloric acid results in a mixture of ortho- and para-substituted aniline derivatives.[125]



Under similar conditions, *N*-phenyl-2-nitrobenzenesulfenamide gives a mixture of 2- and 4-aminodiphenyldisulfides, phenothiazine, and 2-aminobenzenesulfenanilide.[126]

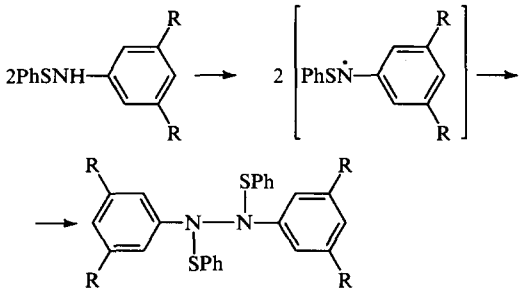
When heated in CCl_4, *N*-methyl-*N*-phenylmethanesulfenamide rearranges into 4-methylthio-*N*-methylaniline.[127]



When 4-nitrobenzenesulfenamide reacts with liquid ammonia in an autoclave, a mixture of 4-nitroaniline, 4,4′-dinitrodiphenyldisulfide, and 4-nitrothiophenol is formed.[128] In addition to various rearrangements, other transformations of sulfenamides are used in the syntheses of functionally substituted aromatic amines. For example, the treatment of *N*-(4-nitrophenyl)-benzenesulfenamide with di-*tert*-butyl hyponitrite at 40 °C in *tert*-butyl alcohol has been reported[129] to yield a radical

$4\text{-}O_2NC_6H_4\dot{N}SPh$, which transforms to the *N*-nitroaniline under the action of Bu_3SnH. Vicarious nucleophilic substitution of the hydrogen atom in the aromatic nucleus of nitroarenes using *N*-unsubstituted sulfenamides has been described.[130] For example, the amination of nitrobenzene with 1-pyrrolidinocarbonylsulfenamide in DMF in the presence of potassium *tert*-butoxide produces a mixture of 2-nitro- and 4-nitroanilines in yields of 34% and 41.5%, respectively. The amination of 1-nitronaphthalene with benzothiazole-2-sulfenamide in DMSO in the presence of potassium *tert*-butoxide gives a mixture of 2-amino-1-nitro- and 4-amino-1-nitronaphthalenes in 11% and 75% yield, respectively.

Among other nitrogen containing compounds that have been synthesised from sulfenamides, tetrasubstituted hydrazines should be noted; they are formed by dimerisation of thioaminyl radicals generated from sulfenamides.[131,132]

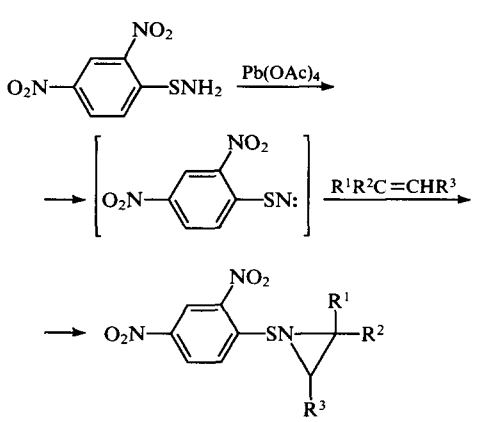


7. Synthesis of heterocyclic compounds

The use of sulfenamides in the synthesis of heterocyclic compounds is mainly based on the following transformations: a) generation of highly reactive intermediates and their reactions with unsaturated compounds; b) thermal rearrangements of sulfenamides; and c) various cyclisation reactions of sulfenamides.

a. Generation of highly reactive intermediates and their reactions with unsaturated compounds

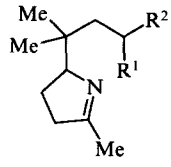
Generation of nitrenes. The generation of nitrenes from *N*-unsubstituted sulfenamides followed by their reactions with alkenes is one methods for the synthesis of *N*-arylthioaziridines.[133-135] Nitrenes are generated in situ by the action of lead tetraacetate on *N*-unsubstituted sulfenamides that contain strong electron-acceptor groups at the sulfur atom, such as 2,4-dinitrophenyl.



R^1 = H, Me, Ph, $H_2C{=}CH_2$; R^2 = H, Me, Ph; R^3 = H, Me

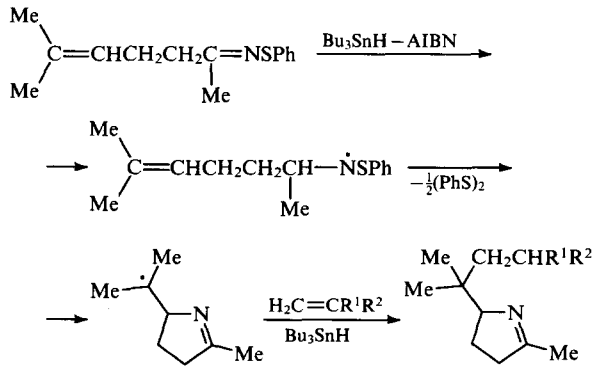
It is noted[133,135] that 2,4-dinitrobenzenesulfenamide is oxidised by lead tetraacetate in the presence of (*Z*)-phenylpropene to give a mixture of *trans*- and *cis*-1-(2,4-dinitrophenylsulfenyl)-2-methyl-3-phenylaziridines, their ratio being dependent on the nature of solvent, on the ratio of the reactants, and on the order of mixing the reagents.[133,135] For example, in benzene, the ratio of *trans*- and *cis*-isomers is 1 : 1, while in chloroform and dichloromethane it is 3 : 1. In more polar solvents (MeCN, MeOH), the overall yield of both isomers decreases. If lead tetraacetate is added to a mixture of 2,4-dinitrobenzenesulfenamide and (*Z*)-phenylpropene, *N*-(2,4-dinitrophenyl)-2,4-dinitrobenzenesulfenamide is formed together with aziridines, and partial isomerization of (*Z*)-phenylpropene to (*E*)-phenylpropene is observed. However, the addition of a mixture of 2,4-dinitrobenzenesulfenamide and lead tetraacetate in chloroform to (*Z*)-phenylpropene results only in high yields of aziridines. The oxidation of 2,4-dinitrophenylsulfenamides is assumed[133] to produce initially a triplet nitrene in equilibrium with the singlet one, both of which react with (*Z*)-phenylpropene. This concept is supported by the fact that the introduction of $4\text{-}ClC_6H_4SCH_2CH{=}CH_2$, which is an efficient trap for singlet nitrenes, into the reaction mixture changes both the overall yield of aziridines and the ratio of isomers, while in the presence of efficient traps for triplet nitrenes, e.g. alkenes, $PhC(R){=}CH_2$ (R = Ph, Me), the ratio of *cis*- and *trans*-isomers does not change, while the overall yield of aziridines decreases.

Generation of iminyl radicals. The generation of iminyl radicals from sulfenamides containing C=N and C=C bonds, and their subsequent addition to alkenes, is the basis for the synthesis of various pyrrolines. For example, a preparative method of synthesis of the pyrroline system is described[136] which involves the interaction of sulfenamide $Me_2C{=}CHCH_2{-}CH_2C(Me){=}NSPh$ with the alkenes $H_2C{=}CR^1R^2$ (R^1 = H, $COOBu^t$; R^2 = COOMe, $COOBu^t$, CN) in the presence of Bu_3SnH–azobis(isobutyronitrile) (AIBN).

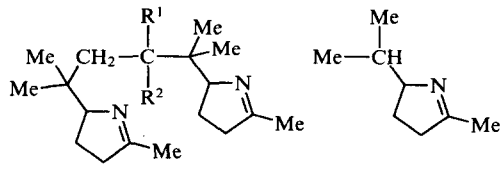


R^1 = H, $COOBu^t$;
R^2 = COOMe, $COOBu^t$, CN

It is supposed[136] that the iminyl radical generated from the sulfenamide is transformed, via cyclisation, to the carbon-centred pyrrolinyl radical whose addition to the alkenes gives the final product.

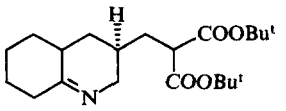


In this case, inconsiderable amounts of the products of the double addition of the primary pyrroline system to alkenes are formed, as well as the products of its stabilisation without subsequent addition.

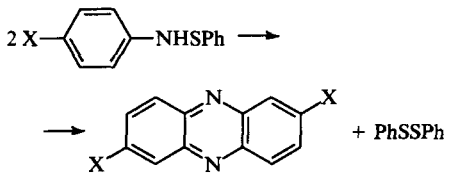


Similarly, when the sulfenamide $H_2C{=}CHCH_2{\cdot}CH(CH_2)_4C{=}NSPh$ reacted with $H_2C{=}C(COOBu^t)_2$ in the

presence of $Bu_3SnH-AIBN$,[136] the heterocyclic ester was isolated as the main product.

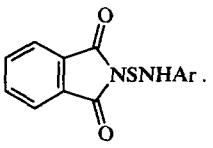


The transformation of 4-substituted *N*-(aryl)benzenesulfenamides into phenazine derivatives in the presence of lead tetraacetate or upon electrolysis is also assumed to occur via iminyl radicals.[34]

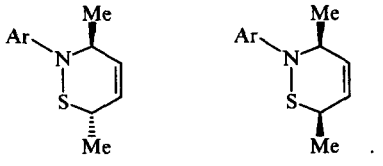


X = Me, Cl, OMe

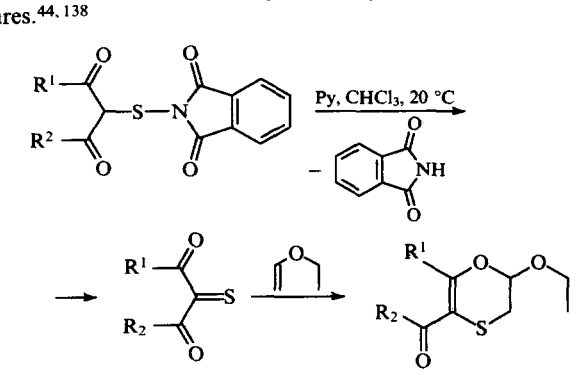
Generation of thionitroso compounds. A method for the synthesis of *N*-substituted derivatives of 1,2-thiazine has been described,[137] which involves the cycloaddition of dienes, (*E*,*E*)- and (*E*,*Z*)-MeCH=CH−CH=CHMe, to arylthionitroso compounds ArN=S (Ar = 4-$MeOC_6H_4$, 4-BrC_6H_4, 4-MeC_6H_4, 4-ClC_6H_4), obtained upon the action of triethylamine in acetone on sulfenamides



The cycloaddition occurs with retention of configuration of the initial dienes, and the following products are obtained, respectively:



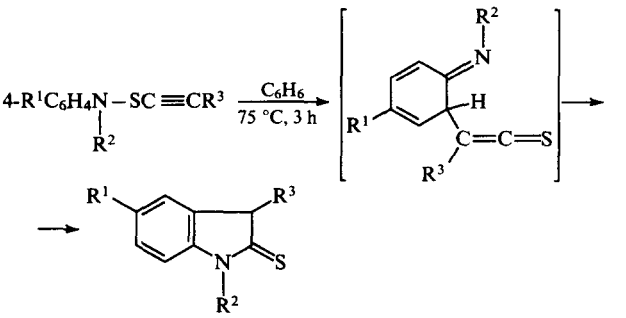
Generation of thiones. In the presence of organic bases, sulfenamides with β,β′-dicarbonyl fragments at the sulfur atom relatively readily transform into α,α′-dioxothiones. The latter undergo Diels–Alder type reactions with unsaturated compounds to yield various cyclic products.[138] A convenient preparative method for the synthesis of some 5,6-dihydro-1,4-oxathiine derivatives has been developed taking into account these features.[44,138]



R^1 = Me, R^2 = MeO (70%); R^1 = 4-$MeOC_6H_4$, R^2 = SPh (87%)

b. Thermal rearrangements of sulfenamides

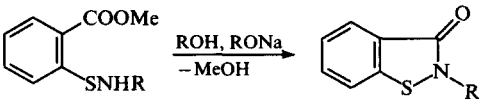
Sulfenamides containing ethenyl and ethynyl fragments at the sulfur atom are usually prone to thermal rearrangement resulting in heterocyclic systems. For example, heating of the sulfenamide Ph(Me)C=NSCH=CH_2 for 40 h in 1,2-diethoxyethane under nitrogen flow gives a 40% yield of 2-phenyl-pyrrole.[12] Under similar conditions, the sulfenamide cyclo-C_6H_{10}=NSCH=CH_2 gives 4,5,6,7-tetrahydroindole in 60% yield.[12] Upon heating in toluene, *N*-(1-naphthyl)-ethenesulfenamides undergo a [3,3]-sigmatropic rearrangement with subsequent elimination of hydrogen sulfide and formation of 1-R-1*H*-benz[*g*]indoles (R = H, Me).[139] Similar rearrangement with subsequent cyclisation occurs upon heating *N*-aryl-1-alkynesulfenamides in anhydrous benzene in an argon atmosphere.[140]



R^1 = H, Me; R^2 = Me; R^3 = Me, Me_3Si

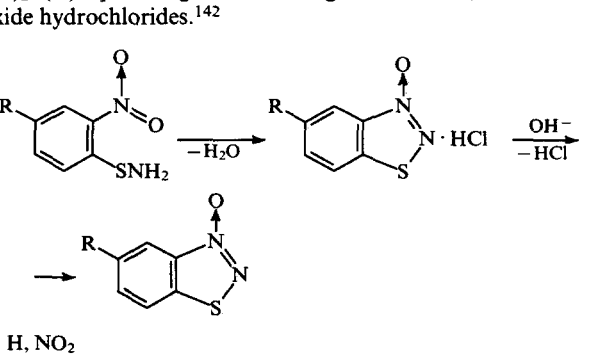
c. Cyclisation reactions of sulfenamides

The possibility of cyclisation of sulfenamides to heterocyclic systems depends on several factors, and mainly on the nature and the structure of substituents at the sulfur and nitrogen atoms, their mutual arrangement, as well as the lability of the S–N and of other bonds in the molecule. Taking into account these factors, preparative synthetic methods for various heterocyclic systems have been developed. For example, *N*-monosubstituted arenesulfenamides containing the alkoxycarbonyl group in the ortho position have successfully been used for the synthesis of 1,2-benzothiazole derivatives. Intramolecular cyclisation of such sulfenamides occurs relatively readily in alcoholic media in the presence of alkoxides.[141]



R = Me, Et, Pr, $PhCH_2$, 4-$MeOC_6H_4$

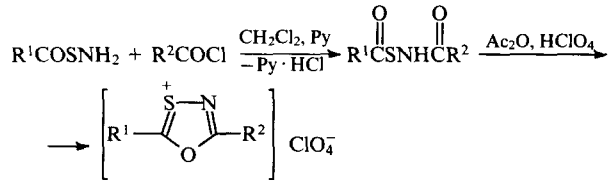
Intramolecular cyclisation of *N*-unsubstituted arenesulfenamides containing the nitro group in the ortho-position occurs in the presence of phosphorus acid chlorides [$POCl_3$, $PhOP(O)Cl_2$, $(PhO)_2P(O)Cl$] and organic bases to give benzo-1,2,3-thiadiazole 3-oxide hydrochlorides.[142]



R = H, NO_2

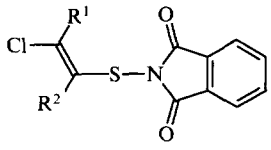
A simple and efficient method for the synthesis of 1,3,4-oxathiazolium perchlorates has been described [143] that involves the

cyclisation of *N*-(acyl)arenecarbonylsulfenamides in acetic anhydride in the presence of 70% $HClO_4$.

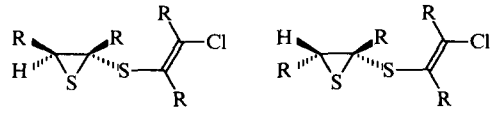


R^1 = 4-$MeOC_6H_4$; R^2 = Me, Ph, 4-$MeOC_6H_4$

Sulfenamides

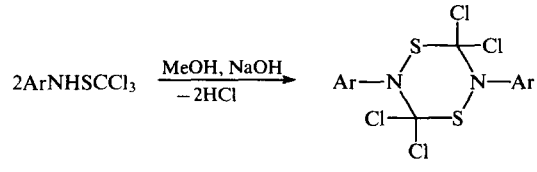


(R^1 = H, Me, Et, R^2 = Me, Et, Bu^t) form[144] a diastereomeric mixture (93 : 7) of thiirane derivatives when treated with 2 equiv. of $LiEt_3BH$, $NaBH_4$, or $LiAlH_4$ in THF at −78 °C.



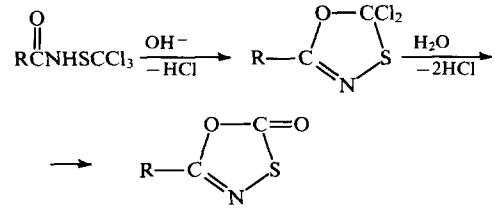
R = Me, Et

Owing to the high reactivity of the trichloromethyl group a rather wide range of methods for the synthesis of various heterocycles has been developed based on *N*-substituted trichloromethanesulfenamides. For example, *N*-(aryl)trichloromethanesulfenamides cyclise in the presence of alcoholic alkali to give 2,5-diaryl-3,3,6,6-tetrachloro-2,3,5,6-tetrahydro-1,4,2,5-dithiadiazines.[8,38]



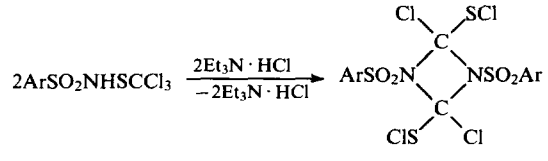
Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$

Under the action of bases (NaOH, EtONa, Et_3N, Py), *N*-(acyl)trichloromethanesulfenamides cyclise to form 5-R-1,3,4-oxathiazol-2-ones.[145,146]

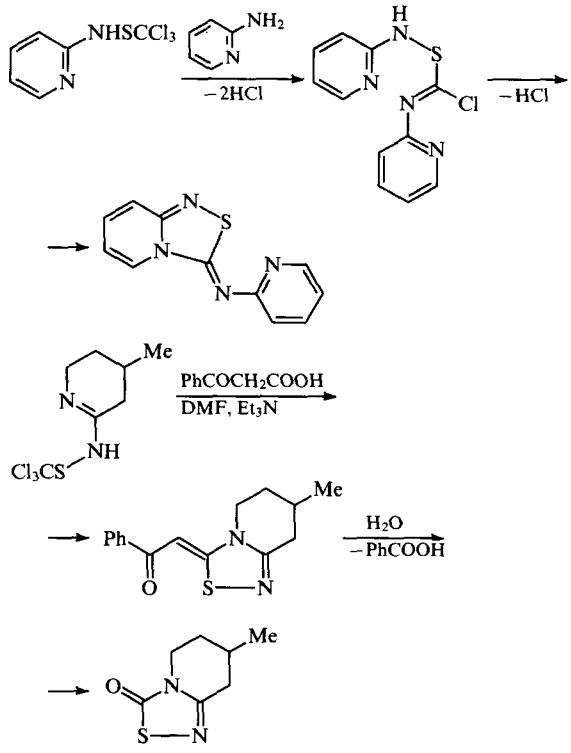


R = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 3-$MeOC_6H_4$, 3,5-$Me_2C_6H_3$

In the presence of triethylamine, *N*-(trichloromethylthio)arenesulfonamides are converted into 2,4-dichloro-2,4-bis(chlorothio)-1,3-bis(arylsulfonyl)-1,3-diazetidines.[8]



A series of 1,2,4-thiadiazole derivatives have been synthesised by the reaction of *N*-(pyrid-2-yl)- and *N*-(tetrahydropyrid-2-yl)trichloromethanesulfenamides with 2-aminopyridine[147,148] or benzoylacetic acid.[149]

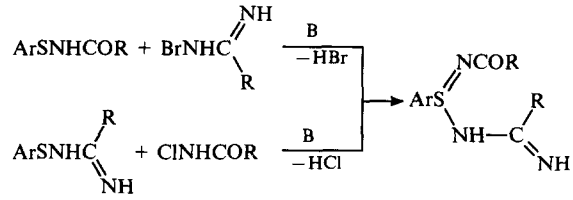


A considerable number of sulfur – nitrogen-containing heterocyclic compounds were obtained by reactions of trichloromethanesulfenyl chloride with various nitrogen-containing compounds, without isolating the intermediate *N*-substituted trichloromethanesulfenamides. Methods for the synthesis of these heterocycles are described in detail in a review[8] and in the literature cited therein.

8. Synthesis of iminosulfur compounds

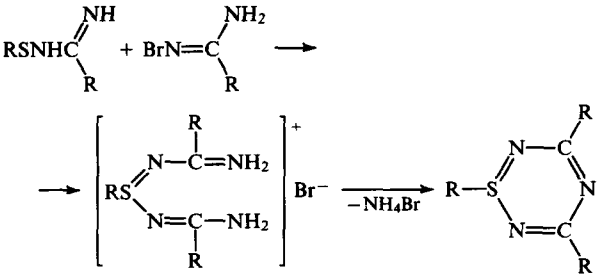
a. Synthesis of amides of sulfinimidic acid

Several methods for the synthesis of amides of sulfinimidic acids based on sulfenamides have been developed. One of the most common methods is based on oxidative imination of sulfenamides with *N*-halo compounds. The main advantage of this method is its one-step character, as well as the possibility of synthesising amides of sulfinimidic acids of varying structure by altering the nature of both the sulfenamide and the iminating reagent. For example, the amides of arenesulfinimidic acids containing acyl and carboximidoyl groups at the nitrogen atoms can be obtained by oxidative imination of *N*-(acyl)arenesulfenamides with *N*-bromoamidines, or by oxidative imination of *N*-(carboximidoyl)arenesulfenamides with *N*-chlorocarboxamides.[150]



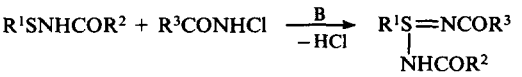
Ar = 4-$O_2NC_6H_4$; R = Me, Ph

N-Bromoamidines also react relatively readily with *N*-(carboximidoyl)sulfenamides to give salts of *N*,*N*′-bis-(carboximidoyl)amides of sulfinimidic acids which form triazines upon heating.[151,152]



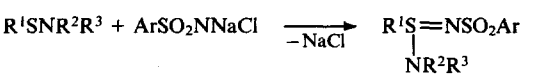
R = Alk, Ar

A series of amides of sulfinimidic acids containing the same or different acyl groups at the nitrogen atoms was obtained by the oxidative imination of *N*-(acyl)sulfenamides with *N*-chlorocarboxamides in the presence of organic bases (RONa, Py, Et_3N).[153,154]

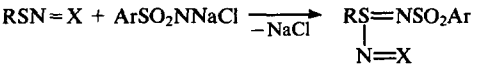


R^1 = 4-$O_2NC_6H_4$, CCl_3;
R^2 = Me, Et, Ph, 4-MeC_6H_4, $PhCH_2$, NH_2, PhNH;
R^3 = Me, Ph

Several amides of sulfinimidic acids containing arylsulfonyl groups were synthesised from sulfenamides and sodium *N*-chlorosulfonamides.[19,20,35,65,146,155–163]

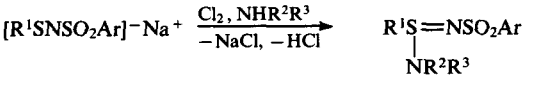


R^1 = Ar, Me, CH_2Cl, $EtOCCl_2$, CCl_3, CCl_2F, CF_2Cl;
R^2 = H, Alk, Ar, Ac, $ArSO_2$, CN; R^3 = H, Alk, Ar



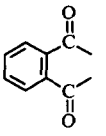
R = Ar; X = $S(O)Ph_2$, $C(OMe)NH_2$, $C(OEt)NH_2$, $C(SEt)NH_2$, $C(NH_2)NH_2$

Yet another method of synthesis of amides of sulfinimidic acids from sulfenamides involves chlorination of sodium *N*-(arylthio)arenesulfonamides with chlorine in the presence of *N*-nucleophiles.[164–166]

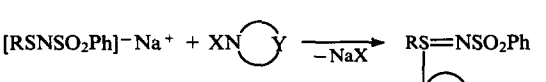


R^1 = 2-$O_2NC_6H_4$, 2,4-$(O_2N)_2C_6H_3$;

R^2, R^3 = Et, C_5H_{11}, iso-C_5H_{11}; R^2+R^3 =

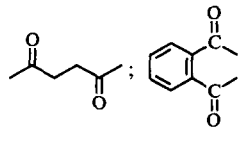


The reaction of sodium *N*-(arylthio)arenesulfonamides with *N*-haloimides is one of the modifications of this method.[166,167]

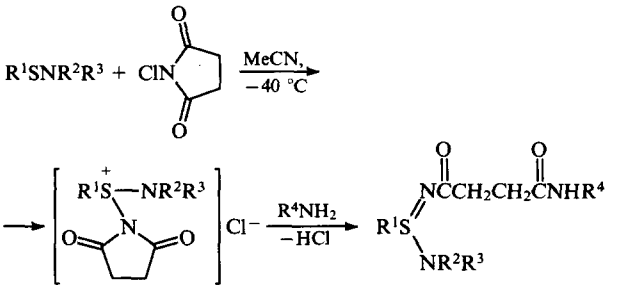


R = 2-$O_2NC_6H_4$, 4-$O_2NC_6H_4$; X = Cl, Br;

Y =



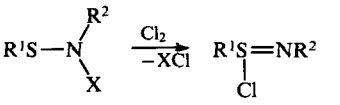
The reaction of *N,N*-dialkylsulfenamides with *N*-chlorosuccinimide gives sulfonium salts which form amides of sulfinimidic acids in the presence of amines.[168]



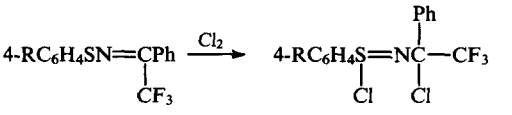
R^1 = Alk, Ar; R^2 = R^3 = R^4 = Alk

b. Synthesis of sulfinimidoyl chlorides

Sulfinimidoyl chlorides are obtained by oxidative chlorination of sulfenamides containing N–H, N=C, N–Si, and N–Na groups, usually in anhydrous aprotic organic solvents.[169–174]

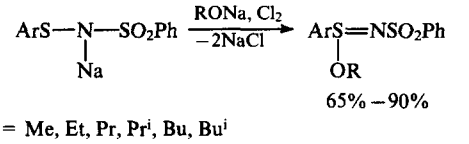


R^1 = Ar, CF_3; R^2 = $ArSO_2$, ArCO, CF_3S, Me_3Si, Bu^t;
X = H, Na, Me_3Si



c. Synthesis of alkyl sulfinimidoates

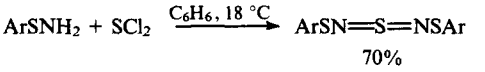
A simple and efficient method of synthesis of alkyl *N*-(arylsulfonyl)sulfinimidoates has been developed, which involves the chlorination of sodium *N*-(arylthio)arenesulfonamides with *tert*-butyl hypochlorite or chlorine in alcoholic media.[175–177]



R = Me, Et, Pr, Pr^i, Bu, Bu^i

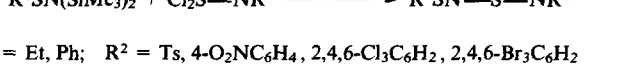
d. Synthesis of sulfurdiimines

N-Unsubstituted arenesulfenamides react with sulfur dichloride in anhydrous benzene to yield *N,N'*-bis(arylsulfenyl)sulfurdiimines.[178]



Ar = 4-$O_2NC_6H_4$

Sulfurdiimines are obtained in the reaction of *N,N*-bis(trimethylsilyl)sulfenamides with *N*-substituted *S,S*-dichlorosulfinimides.[179]

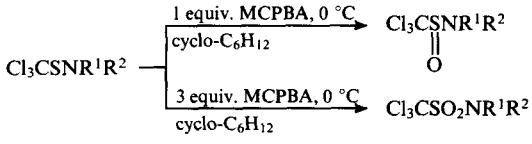


R^1 = Et, Ph; R^2 = Ts, 4-$O_2NC_6H_4$, 2,4,6-$Cl_3C_6H_2$, 2,4,6-$Br_3C_6H_2$

N,N'-Bis(2,4,6-tri-*tert*-butylphenyl)sulfurdiimine resulted from the reaction of 2,4,6-tri-*tert*-butylbenzenesulfenamide with lead tetraacetate.[180]

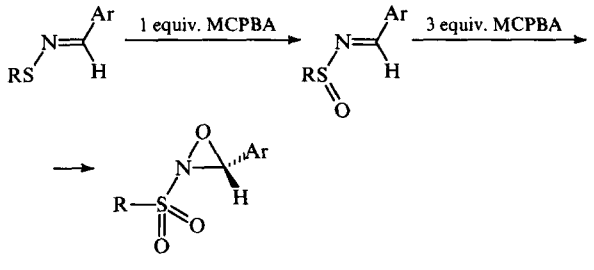
9. Synthesis of sulfin- and sulfonamides

The oxidation of sulfenamides can yield either sulfin- or sulfonamides, depending on the nature of the sulfenamide and the oxidant, on their ratio, and on the oxidation conditions. Manganese dioxide,[181] *m*-chloroperbenzoic acid (MCPBA),[182-184] *N*-chlorosuccinimide,[185] *N*-chlorobenzo-triazole,[186] and other reagents[184] are generally used as the oxidants. MCPBA is the most common oxidising reagent for the synthesis of sulfin- and sulfonamides from sulfenamides. The use of 1 equiv. of MCPBA yields sulfinamides, while three or more equivalents of the oxidising reagent are required for the preparation of sulfonamides, as exemplified by the oxidation of *N*,*N*-disubstituted trichloromethanesulfenamides.



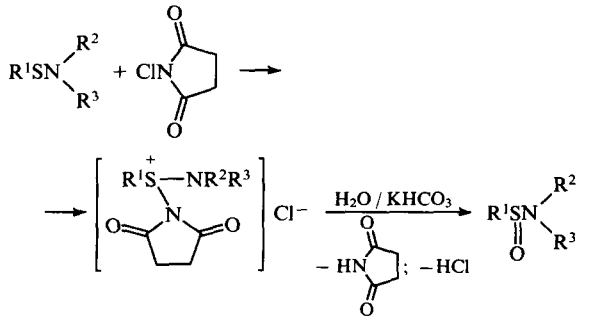
R^1 = Alk; R^2 = Alk, Ar

The oxidation of *N*-arylalkylidenesulfenamides with 1 equiv. of MCPBA results in *N*-sulfinylimines, while a large excess of MCPBA leads to *N*-alkylsulfonylaziridines of (*E*)-configuration.[34]



R = Me, Bu, $PhCH_2$

The oxidation of 6-ethoxybenzothiazole-2-sulfenamide to the corresponding sulfonamide has been shown[184] to occur smoothly in the presence of MCPBA, while the use of hydrogen peroxide or *tert*-butyl hypochlorite is accompanied by oxidation of the heterocycle. The reaction of sulfenamides with *N*-chlorosuccinimide proceeds via the intermediate succinimidosulfonium salt.[185]

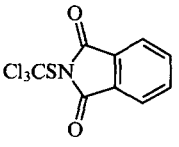


Optically active sulfinamides are obtained by oxidation of the corresponding sulfenamides with *N*-chlorobenzotriazole in the presence of L-menthol or D-tartrate.[186]

IV. Practical application of sulfenamides

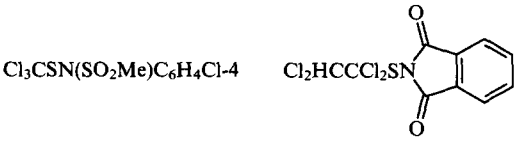
1. Biological activity of sulfenamides

After the first reports on the biological activity of sulfenamides,[187] investigations in this area began to develop intensely. Many patents and scientific papers devoted to this problem have been published. An analysis of the results obtained has been partially reviewed.[8,23,24,188,189] The main achievements involve: the discovery of the fungicidal activity of some sulfenamides, the development of technology for the manufacture of highly effective sulfenamide-based fungicides, and their application in agriculture. The *N*-(trichloromethyl)thiophthalimide, Phthalan, is one of the most valuable fungicides of this series.[190,191]

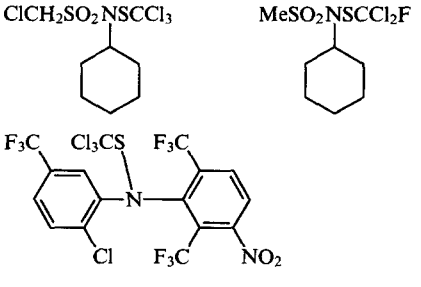


This sulfenamide is widely used as a standard fungicide, against the diseases of apples and pears (tetter), stone-fruits (leaf spots), grapes (mould, anthracnose, red-rot, black, white, and grey rot), gooseberries and currants (anthracnose), tomatoes and potatoes (phytophthora infection).

N-Trichloromethylthio-1,2,5,6-tetrahydrophthalimide (commercial name Kaptan) is also a very valuable fungicide.[190,191] It is widely used against diseases of apples, pears, stone-fruits, strawberries, berry bushes, grapes, tomatoes and potatoes. Mesulfan[190] and Difolathan[190] are characterised by the same fungicidal properties.

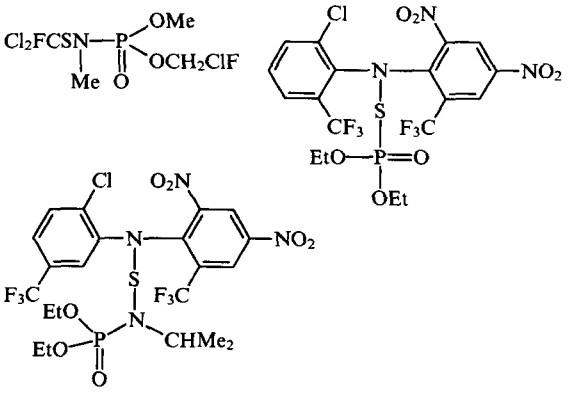


The sulfenamides $FCl_2CSN(Ph)SO_2NMe_2$ (Euparen) and $FCl_2CSN(SO_2NMe_2)C_6H_4Me$-4 (Euparen-M) are also effective fungicides.[191,192] They are used against the diseases of apples, currants, and grapes. The sulfenamides

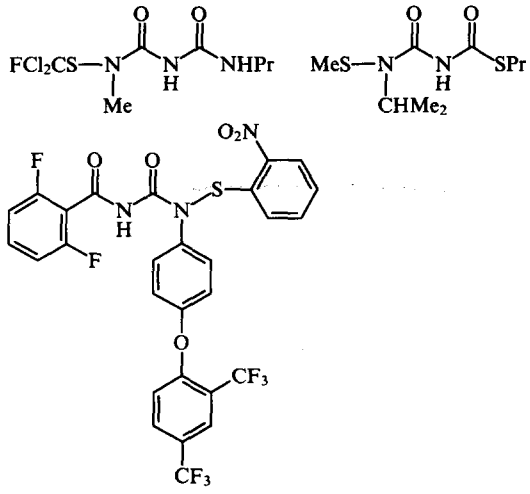


appear to have similar fungicidal properties.[34,193,194]

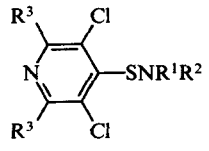
Some phosphorus-containing sulfenamides also exhibit rather high fungicidal activity,[34,195-197]



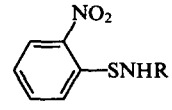
as well as some derivatives of sulfenylurea[198,199] which in addition display insecticidal activity.[200]



Some *N*-substituted 4-pyridinesulfenamides[201] and 2-nitrobenzenesulfenamides[202] exhibit herbicidal, insecticidal, and nematocidal activity.

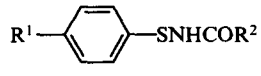


$R^1 = R^2 = H$, Me, Et, etc.; $R^3 = F$, Cl



R = H, 2-$O_2NC_6H_4S$, PhCO, $PhSO_2$

The sulfenamides of the general formula



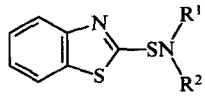
R^1 = H, Cl, NO_2; R^2 = Me, EtO, Ph.

are plant growth regulators.[203]

2. Sulfenamides in the rubber industry

In the rubber industry, sulfenamides are mainly used to accelerate the process of rubber vulcanisation[34,204,205] owing to the high lability of the S–N bond and to its relatively easy homolysis to yield sulfenyl radicals that participate in the vulcanisation processes. Sulfenamides meet all the main requirements for industrial vulcanisation accelerators. In addition to intensification of the process, sulfenamides affect the structure of the resulting cross-linked structures, thus largely predetermining the mechanical properties of the rubber.

2-Benzothiazolesulfenamides are efficient accelerators of rubber vulcanisation;[204,205] they have found wide industrial application.



For example, *N*,*N*-(diethyl)benzothiazole-2-sulfenamide ($R^1 = R^2 = Et$) is an efficient delayed action accelerator at the beginning of vulcanisation. It provides the rubber with strong resistance to ageing and good elasticity. In particular, it is very efficient for rubber working under hard, dynamic conditions.

N-(*tert*-Butyl)benzothiazole-2-sulfenamide ($R^1 = H$, $R^2 = Bu^t$) is also an efficient delayed action accelerator. It results in rubber with strong resistance to ageing, and is used for the production of protectors and carcass rubber.

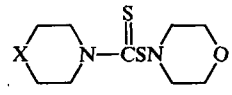
N,*N*-(Diisopropyl)benzothiazole-2-sulfenamide ($R^1 = R^2 = Pr^i$) is used as markedly delayed action accelerator which increases the resistance of rubber mixtures to prevulcanisation as well as to ageing.

N-(*tert*-Octyl)benzothiazole-2-sulfenamide ($R^1 = H$, $R^2 = Me_3CCH_2CMe_2$) is characterised by distinct delayed action at the beginning of vulcanisation. It prevents rubber mixtures undergoing premature vulcanisation.

N-(Cyclohexyl)benzothiazole-2-sulfenamide ($R^1 = H$, $R^2 = cyclo\text{-}C_6H_{11}$) is a very efficient delayed action accelerator at the beginning of vulcanisation. It provides rubber of high elasticity and increased tensile strength as well as good durability. This accelerator is used for the manufacture of protectors and tyre carcasses. *N*-(Hexamethylene)benzothiazole-2-sulfenamide [$R^1 + R^2 = -(CH_2)_6-$], as well as benzothiazole-2-sulfeno morpholide and -(2,6-dimethylmorpholide) [$R^1 + R^2 = (CH_2CH_2)_2O$ and $(CH_2CHMe)_2O$, respectively], display analogous functional activity.

N,*N*-(Dicyclohexyl)benzothiazole-2-sulfenamide ($R^1 = R^2 = cyclo\text{-}C_6H_{11}$) is also a pronounced delayed action accelerator at the initial stage of vulcanisation and provides rubber mixtures of high elasticity and strong resistance to ageing. This accelerator is used in the manufacture of tyres, transporters, shock absorbers, etc.

The thiocarbonylsulfenamides of the general formula



X = O, CH_2.

are even more efficient vulcanisation accelerators than the benzothiazole-2-sulfenamides.[206,207]

The sulfenamides $RSN(X)SO_2Ph$ [X = S(R) = NSO_2Ph; R = Ph, 4-MeC_6H_4, benzoxazolyl] have proved to be efficient accelerators of vulcanisation of butadiene–nitrile rubber 'SKN-26'.[208,209]

Sulfenamides are also used, but not so often, as vulcanisation inhibitors to prolong the prevulcanisation period.[210–213] Usually, *N*-substituted sulfenamides with acyl, arylsulfonyl, and other substituents display these properties.

3. Sulfenamides in the chemistry of polymers

To protect polymers from oxidative degradation specific antioxidants are introduced into polymers. They not only prevent oxidation, but often suppress other undesirable processes favoured by oxygen or peroxides. According to the generally accepted mechanism of oxidant activity,[214] their main role is to bind the active radicals R˙, RO˙, ROO˙, HO˙ formed under the action of oxygen. This results in stable substances or stabilised radicals, X˙, that cannot attack a new polymeric chain.

$$R^{\cdot} + HX \longrightarrow RH + X^{\cdot}$$

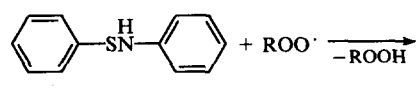
$$RO^{\cdot} + HX \longrightarrow ROH + X^{\cdot}$$

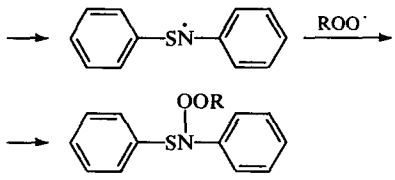
$$ROO^{\cdot} + HX \longrightarrow ROOH + X^{\cdot}$$

$$HO^{\cdot} + HX \longrightarrow HOH + X^{\cdot}$$

$$X^{\cdot} + X^{\cdot} \longrightarrow X{-}X$$

If we take these criteria into account, sulfenamides can be considered as potential polymer antioxidants. Similar to the secondary amines used as industrial antioxidants,[214] *N*-monosubstituted sulfenamides are prone to eliminate a hydrogen atom from the nitrogen atom to produce aminyl radicals; this process can occur in the presence of peroxide radicals.

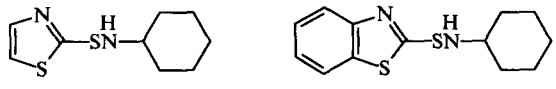




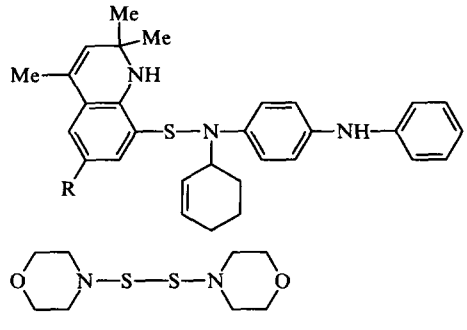
On the other hand, the presence of bivalent sulfur in the sulfenamide molecule, which is able to pass to a higher valence state in the presence of oxidants, should favour the antioxidative properties. Hence, *N*-(cyclohexyl)pentachlorobenzenesulfenamide has been proposed as an antioxidant for polyolefins.[215]

One serious problem hindering the processing of poly(vinyl chloride) is its thermal instability. Thermal destruction of poly(vinyl chloride) occurs in a temperature range of 130–170 °C, while the plastic state which is necessary for processing is reached at a temperature higher than 200 °C.[216] The processing of poly(vinyl chloride) is therefore performed after it has been stabilised. The destruction process of this polymer is rather complicated and has not yet been entirely studied. However, radicals are assumed to play the main role in this process.[214,215] The destruction is initiated by the R˙ radical, which is formed from admixtures or from the polymer itself upon heating.

During degradation, the initially colourless poly(vinyl chloride) first turns yellow, then orange, brown, and black depending on the concentration of conjugated double bonds, which, in turn, depends on the extent of the degradation. It is supposed[214] that HCl liberated is a catalyst of this process, and the role of thermostabilisers is to bind it. However, another mechanism of action of thermostabilisers involving a capture of R˙ radicals and their transformation into inactive products at the beginning of the initiation, should not be excluded. Apparently, the thermostabilisation of poly(vinyl chloride) in the presence of some *N*-substituted sulfenamides occurs according to this scheme. Thus, high thermostabilising activity of *N*-(cyclohexyl)thiazole-2- and benzothiazole-2-sulfenamides towards poly(vinyl chloride) has been reported.[215]

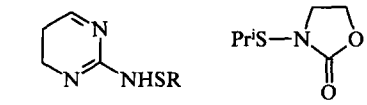


The following sulfenamides have been proposed to thermostabilise halogenated butyl rubber.[215]



4. Sulfenamides as pharmaceuticals

Some sulfenamides are potential pharmaceuticals. Thus, sulfenamides of the pyrimidine series have proved to be antihemorrhagic inhibitors of lipoxygenase and hinder leukocyte migration.[217,218] The oxazolidinone sulfenamide has been described[219] which, in addition to the above mentioned properties, also displays antiasthmatic activity.



R = Ph, Pr^i

3-Nitropyridine-2-sulfenamide and its analogues display antitumour activity.

5. Sulfenamides as electrolytic additives

The application of *N*-phenylthio-*N*,*N*′-bis(phenylsulfonyl)benzenesulfinamidine as an additive to the electrolyte for silver plating of metals was shown to improve the coating quality.[220] The use of this electrolyte provides coatings with fine crystal structure, lustre, and good adhesion to a support.

* * *

Thus, application of sulfenamides in fine organic synthesis is based on the specific features of their structure and reactivity, namely the presence of two active centres (S and N) and the high lability of the S–N bond. The capability of this bond to be relatively easily cleaved in the presence of both nucleophilic and electrophilic reagents, as well as to be homolysed, enables sulfenamides to be used as carriers of the sulfenyl group in syntheses of sulfides, disulfides, esters of sulfenic acids, and other sulfur-containing compounds, and to be used as a protective function in syntheses of peptides and alkaloids. The ability of sulfenamides to generate various highly reactive intermediates is a property of synthetic importance, which is widely used in syntheses of heterocyclic compounds and various sulfur-imino compounds. The practical application of sulfenamides in the rubber industry, macromolecular chemistry, agriculture, and other areas is of no less importance.

The search for, and development of, unusual methods of sulfenamide synthesis, such as the chlorosulfenylamidation of alkenes and alkynes, sulfenylamidation of CH-acids, etc., seem in the immediate future to be the main directions of research in this field of organic synthesis. The study of the reactions of sulfenamides involving the generation of various highly reactive intermediates should progress considerably. Their employment in organic synthesis will prompt the emergence of new polyfunctional compounds, including potentially valuable ones.

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