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# Sulphenamides and their derivatives

K A Petrov, G V Rudnev, V D Sorokin

ABSTRACT. Information has been presented systematically on the synthesis of sulphenamides and related compounds by reaction of sulphenyl chlorides and sulphur chlorides with amines and carboxylic acid amides; by reaction of chloramines with mercaptans; by transamination of *N*-acylsulphenamides; and by reaction of disulphides with amines. The following chemical reactions of sulphenamides have been examined: reaction with hydrogen halides; with acids and derivatives possessing coordinatively unsaturated atoms; and the addition of sulphenamides to the double bond of carbon disulphide, isocyanates, isothiocyanates and olefins. Data are given on the physical state of sulphenamides and on the region characteristic of the S–N bond vibrations.

The bibliography includes 190 references.

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## I. Introduction

Sulphenamides are important sulphenic acid derivatives which possess a S–N group. The following types of sulphenamide are known: alkyl- and aryl-sulphenamides, *S*-acyl- and *N*-acyl-sulphenamides, sulphenamides derived from the hypothetical sulphoxylic acid, $S(OH)_2$, and thiosulphoxylic acid, $S_2(OH)_2$; and aminosulphenyl chlorides which possess both a S–N bond characteristic of sulphenamides and a S–Cl bond characteristic of sulphenyl chlorides. As the S–N bond is readily cleaved with various reagents, sulphenamides are used in synthetic chemistry for introducing both sulphur and nitrogen functions, affording a variety of sulphides,[1,2] disulphides,[3,4] trisulphides,[5,6] sulphenic acid esters,[7] and other compounds.

Sulphenamides and derivatives are widely used as accelerators in the vulcanisation of rubber,[8–20] in agriculture as pesticides and fungicides,[21–29] for treating the after-effects of radiation sickness, as radio-protecting agents,[30] as polymerisation initiators,[31] and even in rocket technology as spontaneously igniting fuels.[32]

At the present time there is a large volume of data on this subject in foreign publications;[33–37] there is nothing of a review nature with the exception of one article[38] which in part summarises known information.

## II. Methods of preparation

Sulphenamides and related compounds are prepared by amination of sulphenyl halides, sulphenic acid esters, and sulphur chlorides with alkyl- and aryl-amines and with amides; they are also obtained by treatment of mercaptans with chloramines, disulphides with amines, from thiosulphonates and alkylsulphenyl thiocyanates with amines, and by other methods.

### 1. Amination of sulphenyl halides

Zinke was first to prepare sulphenamides in high yield by treatment of sulphenyl chlorides with an excess of secondary amine in chloroform or carbon tetrachloride at low temperature.[33,36,39]

$$R{-}S{-}X + 2HNR^1_2 \rightarrow R{-}S{-}NR^1_2 + HNR^1_2 \cdot HX,$$

$R = Ph,\ O_2N{-}C_6H_4;\ R^1 = Me,\ Et;\ X = Cl,\ Br.$

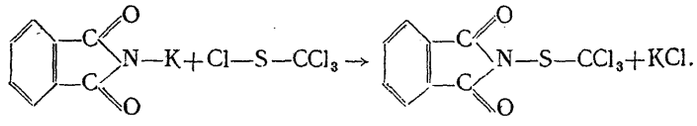
Subsequently, triethylamine[40–42] was used as HCl acceptor in order to economise in the use of the secondary amine. This reaction does not always proceed smoothly with the formation of desired product in high yield. Thus, by treatment of methylsulphenyl chloride with excess of dialkylamine at 60 °C, *gem*-diamines as well as methyldi- and tri-sulphides were obtained together with the desired sulphenamides.[43]

$$Me{-}S{-}Cl + R{-}NH_2 \rightarrow Me{-}S{-}NR_2 + CH_2(NR_2)_2 + Me{-}S_2{-}Me + Me{-}S_3{-}Me,$$

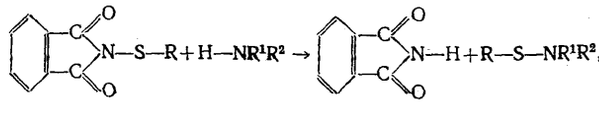
$R = Me,\ Et,\ iso\text{-}Pr.$

By an analogous route, *N*-methylalkanesulphenanilides were obtained by reaction of the corresponding sulphenyl chlorides with *N*-methylaniline, the only difference being the choice of aqueous base as medium. The desired products were isolated in yields up to 70–80% by extraction and distillation.[44]

This method is recommended for low-molecular weight sulphenyl chlorides, i.e. those with small alkyl (R) groups.[45–47] By such means, *N*-acylsulphenamides are obtained in high yield by reaction of *N*-potassiophthalimide with sulphenyl chlorides.



*N*-Acylsulphenamides are converted to deacylated sulphenamides by transamination.[48–50]



$R = Me,\ Et,\ Ph,\ C_6H_4;\ R^1 = Me,\ Et;\ R^2 = Et,\ iso\text{-}Pr.$

Isolation of the desired products is facilitated by the use of non-polar solvents in which phthalimide has low solubility.

Those sulphenamides derived from the hypothetical sulphoxylic and thiosulphoxylic acids, referred to usually as thiobisamines and dithiobisamines or diaminosulphides, are obtained in around 90% yield by interaction of sulphur dichloride with secondary aliphatic, cyclic, and *N*-alkylaryl amines in chlorinated hydrocarbon solvents at low temperature or in aqueous basic medium.[51–60]

$$4R_2NH \begin{cases} \xrightarrow{SCl_2} R_2N{-}S{-}NR_2 + R_2NH\cdot HCl \\ \xrightarrow{S_2Cl_2} R_2N{-}S_2{-}NR_2 + R_2NH\cdot HCl \end{cases}$$

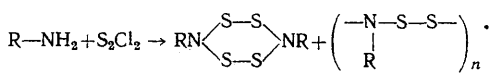
R = Me, Et, Pr, Bu, $(CH_2)_5CH$; $R_2 = (CH_2)_2O(CH_2)_2$, $(CH_2)_5$.

Thiobisamines with a HN–S group are obtained by reaction of primary aliphatic and aromatic amines, in particular *tert*-butylamine and *p*-nitroaniline, with sulphur dichloride in ether.[61,62]

$$R{-}NH_2 + SCl_2 \xrightarrow{ether} RHN{-}S{-}NHR,$$

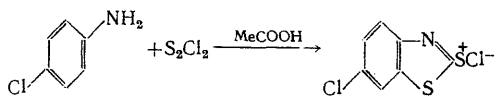
$R = p\text{-}NO_2C_6H_4$, *tert*-Bu.

It is also reported that primary aliphatic amines with sulphur monochloride produce tetrathiodiamines or polymeric disulphides in 40–60% yield.[63,64]



R = Et, Ph–$CH_2$, Ph–$CH_2CH_2$, $C_{12}H_{25}$; $n$=5–9.

As a rule primary aromatic amines react with sulphur monochloride to give a mixture of products, of which compounds with a C–S bond predominate.[65,66] Thus, by heating *p*-chloroaniline with sulphur monochloride in acetic acid during 3 h, yellow crystals of 6-chloro-1,2-dithiazinium chloride were obtained in 93% yield.[67]



Thiobisamines are obtained in high yield by treatment of metallated secondary amines with sulphur dichloride.[68]

$$R^1R^2NLi + SCl_2 \xrightarrow{-78^\circ C} R^1R^2N{-}S{-}NR^1R^2 + LiCl,$$

$R^1 = SiMe_3$; $R^2$ = Bu, *iso*-Pr, *tert*-Bu, $(CH_2)_5CH$.

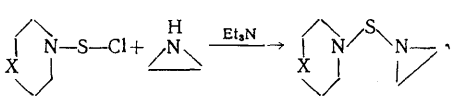
Extremely reactive aminosulphenyl chlorides possessing both sulphenamide and sulphenyl chloride groups are obtained by cleavage of dithiobisamines with chlorine or sulphuryl chloride, as well as by treating thiobisamines with hydrogen chloride.[69,70]

$$R_2N{-}S{-}NR_2 + HCl \rightarrow R_2NSCl + R_2NH\cdot HCl,$$
$$R_2N{-}S_2{-}NR_2 + SO_2Cl_2 \rightarrow 2R_2N{-}S{-}Cl + SO_2,$$

R = Me, Et, *iso*-Pr, *tert*-Bu, $(CH_2)_5CH$;

$R_2 = (CH_2)_2O(CH_2)_2$.

Aminosulphenyl chlorides are used to prepare thiobisamines with a variety of amino groups. For example, unsymmetrical thiobisamines are obtained by treatment of aminosulphenyl chlorides with ethyleneimine in carbon tetrachloride in the presence of tertiary amine at room temperature.[71]



X = O, S, $CH_2$.

At the same time it has been reported that on treatment of diethylaminosulphenyl chloride with dimethylamine, and of dibutylaminosulphenyl chloride with dicyclohexylamine, only symmetrical thiobisamines, namely bis(dimethylamino) sulphide and bis(dicyclohexylamino) sulphide, were isolated in 80% yield. It is thought that this reaction proceeds as a result of disproportionation of an initially formed unsymmetrical thiobisamine under the action of hydrogen chloride.[72]

$$R_2NH \xrightarrow[-HCl]{R^1_2NSCl} R_2N{-}S{-}NR^1_2 \xrightarrow[-HNR^1_2]{HCl}$$
$$\rightarrow R_2NSCl \xrightarrow[-HCl]{HNR_2} R_2N{-}S{-}NR_2,$$

R = Me, $(CH_2)_5CH$; $R^1$ = Et, Bu.

Suphenamides phosphorylated on the sulphur atom are obtained by interaction of aminosulphenyl chlorides with dialkyl or trialkyl phosphites in high yield.[73]

$$R_2N{-}S{-}Cl + (R^1O)_3P \rightarrow (RO)_2\overset{\overset{O}{\|}}{P}{-}SNR_2 + R^1{-}Cl,$$

R = Et; $R^1$ = Et, Pr, Bu.

The isolation of *S*-dialkylamino dialkyl thiophosphates presents no difficulty because the only side-product of the reaction is a volatile alkyl chloride.

An unstable acetylsulphenamide, which decomposes into sulphur and diethylacetamide, was obtained by reaction of acetylsulphenyl chloride with diethylamine.[74]

$$CH_3{-}\overset{\overset{O}{\|}}{C}{-}S{-}Cl + 2(C_2H_5)_2NH \rightarrow$$
$$\rightarrow CH_3\overset{\overset{O}{\|}}{C}{-}S{-}N(C_2H_5)_2 + (C_2H_5)_2NH\cdot HCl.$$
$$\downarrow$$
$$CH_3C(O)N(C_2H_5)_2 + S$$

A similar result was obtained with piperidine. The oily sulphenamide synthesised from aniline at 3–5 °C decomposed by 50% during 24 h and completely during the course of 3 days.

## 2. Amination of mercaptans with chloramines

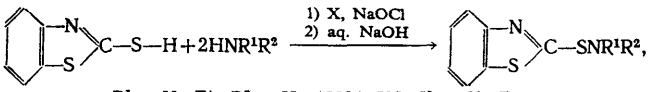
Sulphenamides with a free amino group ($-NH_2$) are obtained in yield up to 50% by reaction of mercaptides with chloramine.[75]

$$R{-}S{-}Na \xrightarrow[2)\ aq.\ NaOH]{1)\ NH_2Cl/H_2O} R{-}S{-}NH_2 + NaCl,$$

R = pyridyl, pyrimidinyl, 1,2-$Cl_2C_6H_3$, $O_2N{-}C_6H_4$.

The reaction was conducted in aqueous basic solution. The sulphenamides were recrystallised from a mixture of petroleum ether and isopropanol. However, if diethyl ether is used as solvent, the corresponding disulphide is formed.

Sulphenamides can also be prepared by the reaction of aromatic mercaptans, notably 2-mercaptobenzothiazoles, with ammonia, or with primary and secondary amines in the presence of hypochlorites, halogens or potassium ferricyanide in aqueous solution.[76–81]



$R^1$ = H, Et; $R^2$ = H, $(CH_2)_5CH$; X = Cl, Br, I.

This method is related to the chloramine route since mercaptans and amines react with chlorine or hypochlorite with formation of sulphenyl chlorides and chloramines, following which the former will interact with the amines and the latter with the mercaptides.

*N*-Acylsulphenamides are also obtained in up to 70% yield by reaction of *N*-chlorosuccinimide and *N*-chlorophthalimide with mercaptans.[82]

$$R^1R^2NCl + HS{-}R^3 \xrightarrow{OH^-} R^1R^2NSR^3,$$

$R^1R^2N$ = succinimido, phthalimido; $R^3$ = Et, *iso*-Pr, Ph.

### 3. Amination of disulphides

One of the methods of preparing sulphenamides is based on the interaction of alkyl or aryl disulphides with primary or secondary amines in the presence of silver acetate, silver nitrate or mercuric chloride. The yield of the sulphenamides is 60–80% by this route.[83]

$$R{-}S_2{-}R + 2R^1_2NH + MX \xrightarrow{NaOH} R{-}S{-}NR^1_2 + R{-}S{-}M + R^1_2NH\cdot HX,$$

R = Me, Et, *iso*-Pr, Bu, Ph; $R^1$ = Me, Et, *iso*-Pr, Bu, Ph;

$MX = AgNO_3$, AgOAc, $HgCl_2$.

It is thought that, initially, a disulphide complex is formed as a result of electrophilic attack of the metal ion; the complex is then decomposed with the formation of sulphenamide as a result of nucleophilic attack by the amine. Reaction is carried out in the following way: equimolar amounts of the disulphide and metal salt in methanol or ethyl acetate are treated with an excess of the amine, the precipitated mercaptide is separated by filtration, and the sulphenamide is isolated from the filtrate by the usual means. Reaction is easiest by using aromatic, as opposed to aliphatic, disulphides, and the yield of the desired sulphenamides is highest. This method is also suitable for preparing sulphenamides with a free $NH_2$ group if the nucleophile which attacks the sulphur atom is more electron-accepting than 4-chlorophenyl; if the reverse obtains, bis(arylsulphenyl)amines are isolated as the main products.[83]

This method possesses a number of distinct advantages by comparison with the route based on sulphenyl chlorides. Firstly, disulphides are more stable than sulphenyl halides, and secondly the method permits the synthesis of sulphenamides which contain reactive functional groups, such as hydroxyl or a double bond, which are reactive towards sulphenyl chlorides.[45,46]

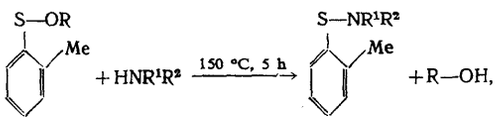
Sulphenamides phosphorylated on the sulphur atom are obtained in high yield by treatment of dithiophosphates with primary and secondary amines.[84]

$$(RO)_2P(O){-}S_2{-}P(O)(OR)_2 + 2HNR^1_2 \rightarrow (RO)_2P(O){-}S{-}NHR^1 + (RO)_2P(O)SH + H_2NR^1,$$

R = Et, *iso*-Pr; $R^1$ = Me, Et, *iso*-Pr.

### 4. Amination of arenesulphenates, alkylsulphenyl thiocyanates and thiosulphonates

Sulphenamides are obtained in high yield by amination of arenesulphenates with primary or secondary amines.[85]




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

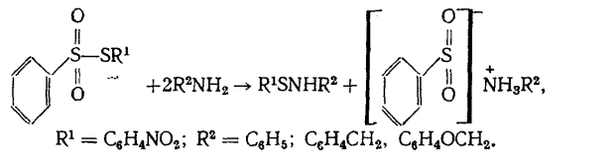
This method is more advantageous than the above-described sulphenyl halide route since sulphenic acid esters are more stable than the corresponding sulphenyl chlorides.

Certain dialkylsulphenamides are obtained by interaction of alkylsulphenyl thiocyanates with a two-fold excess of secondary amine in ether.[86,87]

$$R{-}S{-}S{-}CN + 2R^1_2NH \rightarrow R{-}S{-}NR^1_2 + R^1_2NH\cdot HS{-}CN,$$

R = Et, Pr, Bu; $R^1$ = Et, Pr, *tert*-Bu.

The possibility of aminating thiosulphonates with amines is exemplified by the amination of 2-nitrophenyl benzenethiosulphonate with aromatic amines. In this case, the corresponding *N*-aryl-2-nitrobenzenesulphenamides are isolated in high yield.[88]




$R^1 = C_6H_4NO_2$; $R^2 = C_6H_5$; $C_6H_4CH_2$, $C_6H_4OCH_2$.

In other cases it is not possible to isolate sulphenamides from a mixture of the corresponding thiosulphonate and aromatic amine.

### 5. Other methods of synthesising sulphenamides

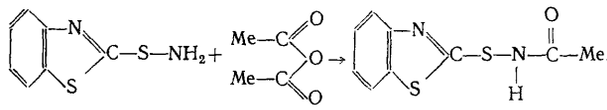
One of these is based on the amination of mercaptides with azides. By this means, treatment of *tert*-butyl or benzyl mercaptan with butyl azidoacetate or azidoformate in the presence of cuprous oxide or cuprous chloride affords the corresponding sulphenamides in 50% yield.[89]

$$R{-}S{-}H \xrightarrow{Cu(I)} Cu{-}S{-}R \xrightarrow[-N_2]{N_3R^1} R^1NHSR + R{-}S_2{-}R + R^1NH_2,$$

R = tert-Bu, $C_6H_4CH_2$; $R^1$ = $CH_2CO_2Bu$, $CO_2Bu$.

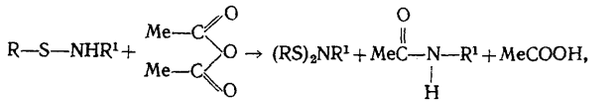
It is proposed[89] that the mechanism of the reaction involves coordination of an intermediate nitrene with the copper atom, followed by insertion of the amino group into the Cu–S bond with formation of sulphenamide, amine and disulphide.

The following method, based on the acylation of sulphenamides with free amino groups, is used for the preparation of acylated 2-benzothiazolylsulphenamides.[90]



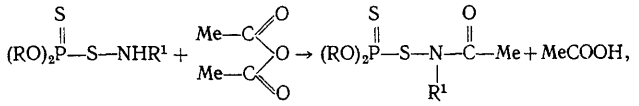

Reaction is conducted in the presence of sodium acetate. In this way, disulphide is formed in addition to acylated product. The desired product was recrystallised from ether. The yield was 30%.

It is known that on acetylation of sulphenamides, the latter are cleaved with the formation of bis-sulphenylamines and the corresponding amide of acetic acid.[91,92]




R = Alk, $R^1$ = Me.

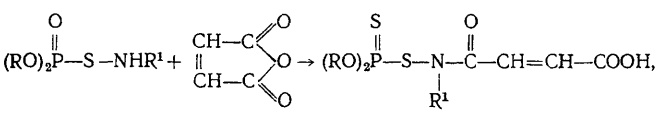
At the same time phosphorylated sulphenamides readily react with acetic anhydride with formation of the corresponding *N*-acetyl derivatives in 72–95% yield.



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

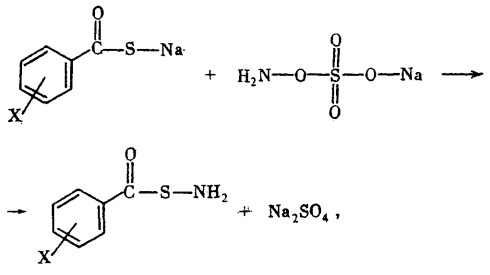
Reaction proceeds at room temperature in the absence of solvent during 30 min, or by vigorous heating of the starting materials up to 100 °C during 2–3 min.

In addition to this, sulphenamides are acylated with maleic anhydride under the same conditions.[93]



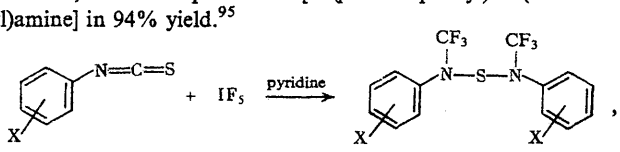
R = Me, Et, *iso*-Pr; $R^1$ = Me.

One of the methods of preparing *S*-acylsulphenamides is by amination of salts of aromatic thioacids with hydroxylamine-*O*-sulphonates. Reaction is conducted by mixing an aqueous solution of sodium hydroxylamine-*O*-sulphonate with the sodium salt of an aromatic thioacid, followed by filtration of the product and recrystallisation from ether, methylene chloride, chloroform or carbon tetrachloride. The yield was around 90%.[94]



X = Cl, $NO_2$, Me, $H_2NSCO$.

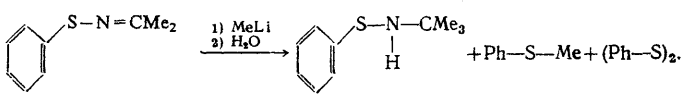
There is a certain interest in the reaction of iodine pentafluoride with phenyl thiocyanates in methylene chloride, leading to the formation of, for example thiobis[*N*-(*p*-chlorophenyl)-*N*-(trifluoromethyl)amine] in 94% yield.[95]



X = Me, Cl, Br, I.

The thiobisamine was isolated from the reaction mixture by column chromatography (eluent: 1 : 1 pentane/methylene chloride).

Sulphenamides can also be obtained by the addition of organometallic compounds to *N*-alkylidenearenesulphenamides, followed by decomposition of the formed products with water. An *S*-phenylsulphenamide was obtained by this route. *N*-Isopropylidenebenzenesulphenamide and methyllithium were used as starting materials.[96]



Reaction was conducted in ether at a temperature around 0 °C; the yield of the sulphenamide was 78%.

## III. Physical properties

Sulphenamides and their derivatives exist as liquids or crystalline compounds with clearly defined melting points. The vast majority are colourless, but some are yellow because of impurities. They have an unpleasant smell and are readily soluble in non-polar solvents (benzene, chloroform, methylene chloride, or hexane).[33–38,69,97–100] The S–N bond order in simple methylated mono- and disulphenamides is significantly greater than one. For example, the bond orders for methylthiodimethylamine, $Me_2NSMe$, and bis(methylthio)methylamine, $MeN(SMe)_2$, and 1.2 and 1.5, respectively.[101] The S–N bond length in unsaturated aliphatic sulphenamides is around 160 pm; for arylsulphenamides it is around 155 pm, and for dithiobisamines the S–S bond length is approximately 195–205 pm. The C–N–S bond angle, around 100°, depends on the nature of the neighbouring atoms and groups.[102–104]

Based on a study of the temperature dependence of the PMR spectra of a series of cyclic and acyclic sulphenamides, it is assumed that inversion at the nitrogen atom is the rate-determining step only for aziridine derivatives.[105,106]

The rotation barrier around the S–N bond in compounds of the type $ArSN(SO_2Ph)Pr$-*iso* is 55–58 kJ $mol^{-1}$, being dependent on the lone pair interaction, the S–N bond order, and the steric effect of the substituents.[107]

From an X-ray structural analysis, it has been established that the bonds to nitrogen lie almost in the same plane as a result of $p_\pi$–$d_\pi$ interaction between the $sp^2$-hybridised nitrogen atom and the electron-donating sulphur atom.[108–110] In the IR spectrum the S–N bond absorbs in the region 640–670 $cm^{-1}$ and 800–900 $cm^{-1}$.[55,111]

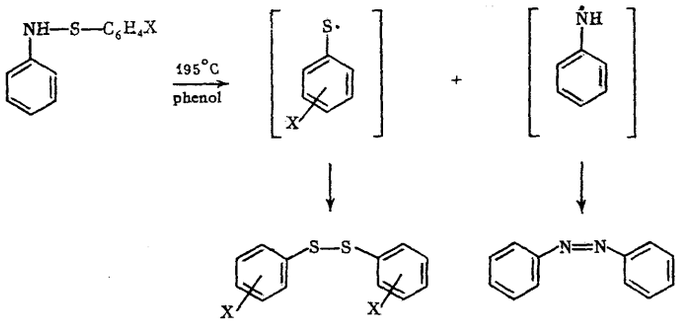
## IV. Chemical properties

Sulphenamides and related compounds with a S–N bond are chemically reactive. Characteristically, their reactions proceed by an ionic mechanism, associated with heterolytic cleavage of the S–N bond. The vast majority of these reactions involve nucleophilic substitution or electrophilic addition to a double bond. Reactions of sulphenamides do not normally follow a radical pathway with heterolytic cleavage of the S–N bond. However, such radical reactions do take place in the vulcanisation of rubber, for which sulphenamides serve as accelerators. These reactions have been studied only in rare instances.

### 1. Thermal decomposition of sulphenamides

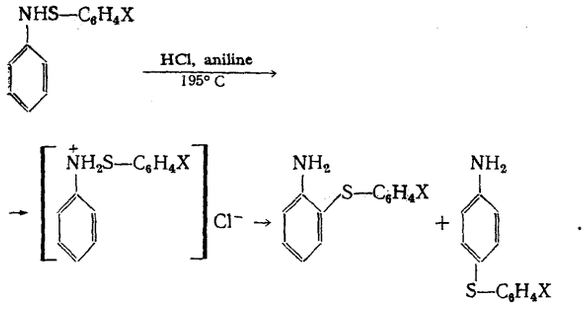
In spite of the widespread use of sulphenamides as accelerators for the vulcanisation of rubber, thermal decomposition of this class of compound has only been studied in the main with arenesulphenamides.[112–114] Thus, on heating sulphenamides to 195 °C, homolysis of the S–N bond takes place with formation of sulphenyl and aminyl radicals, which afford a mixture of disulphide and hydrazobenzene as a result of dimerisation; the hydrazobenzene

then disproportionates to the corresponding azobenzene.[112]

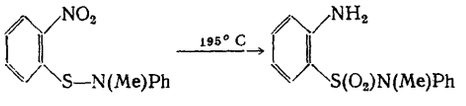


X = Cl, Br, $NO_2$.

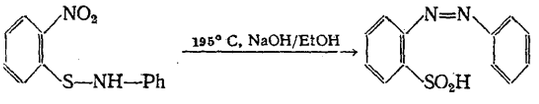
In the presence of acid, a mixture of 2- and 4-aminophenyl aryl sulphide is formed as a result of intramolecular rearrangement of the protonated form of the corresponding sulphenamide.



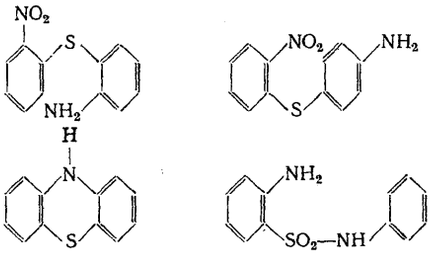
The nature of the solvent has a significant effect on the course of the reaction.[113] Thus, *N*-(2-aminobenzenesulphonyl)-*N*-methylaniline is formed on heating *N*-(2-nitrophenylsulphenyl)-*N*-methylaniline.[115,116]



In ethanolic NaOH, *N*-(2-nitrobenzenesulphenyl)aniline rearranges into an azosulphinic acid.[117]



A mixture of 2- and 4-aminophenyl 2-nitrophenyl sulphide, phenothiazine, and *N*-(2-aminobenzenesulphonyl)aniline was obtained by heating *N*-(2-nitrobenzenesulphenyl)aniline to 195 °C for 15 h in aniline.[118]



Alkylsulphenamides are more unstable than arylsulphenamides. The thermal stability decreases where a neighbouring group exerts an anchimeric effect on S–N bond cleavage (for example, in the presence of an acyl group), and as the basicity of the sulphenamide increases.[38]

## 2. Hydrolysis

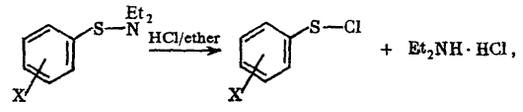
There are no data on the hydrolysis of sulphenamides. Evidently, this is explained by the fact that hydrolysis leads to sulphenic acids which in the large majority of cases are unstable.[33,119] However, a study of the hydrolysis of thiobisamines and dithiobisamines with dilute HCl has been made. Thus it has been shown that hydrolysis of these derivatives affords a mixture of sulphur dioxide, sulphur, hydrogen sulphide and the corresponding amine.[120]

$$RN_2—S_x—NR_2 \xrightarrow{H_2O+HCl} SO_2+H_2S+S+R_2NH,$$
$$R = Me, Et, \textit{iso}\text{-Pr};\ x = 1, 2.$$

It is considered that reaction proceeds via sulphur chlorides which then undergo hydrolysis. Sulphenamides and related compounds are comparatively stable in cold aqueous and aqueous basic media, so that they can be prepared in the latter medium by reaction of sulphenyl chlorides with amines or from chloramines and mercaptides; sulphenamides may also be isolated from complexes by treatment with aqueous base.[37,121]

## 3. Reaction with hydrogen halides

Sulphenamides are readily cleaved with hydrogen halides with formation of sulphenyl halides in high yield.[122–133] The best results are achieved if HCl gas is passed through an ethereal solution of the sulphenamide.[122–130]

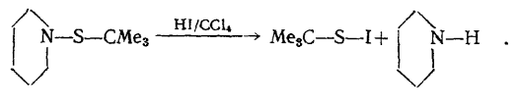


X = H, $NO_2$.

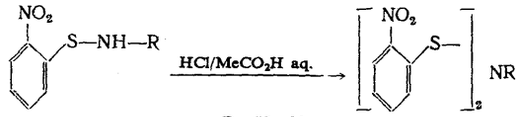
In this way, *o*-nitrobenzenesulphenyl chloride was obtained by using *o*-nitrobenzenesulphenamide. The yields of sulphenyl halide are lower if the sulphenamides are treated with HBr or HI.[127,131] For example, sulphenyl bromides were obtained by treating the corresponding sulphenamides with ethereal HBr at *ca.* 0 °C;[127]

$$R—S—NHR^1 \xrightarrow{HBr/ether} R—S—Br+HNRR^1,$$
$$R = \textit{tert}\text{-Bu}, NO_2C_6H_4;\ R^1 = Me, Et, \textit{iso}\text{-Pr},$$

and *tert*-butylsulphenyl iodide and piperidine were obtained by treatment of a solution of *N*-*tert*-butylthiopiperidine with aqueous HI in carbon tetrachloride.[131]

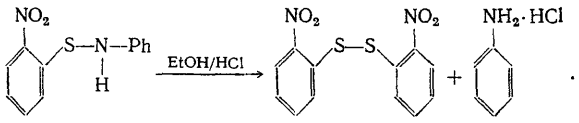


The yields of sulphenyl chlorides are lower if the sulphenamides are cleaved with concentrated hydrochloric acid.[40,134–136] It is also reported that if the derived sulphenyl chlorides are unstable, the corresponding disulphide is obtained; and by heating sulphenamides with dilute hydrochloric or acetic acid, sulphenimides are formed.[136]



R=H, Me.

Only disulphide and aniline hydrochloride are formed on heating the corresponding sulphenanilide in ethanol or in dilute hydrochloric acid.[134,137–139]



Thio- and dithio-bisamines are cleaved at the S–N bond in the same way as sulphenamides by action of anhydrous HCl with the formation of sulphur chlorides and amine salts.[70,120]

$$R_2N{-}S_n{-}NR_2 + 4HCl \xrightarrow{\text{ether, 0 °C}} S_nCl_2 + 2R_2NH\cdot HCl,$$
$$R = Me, Et, Bu;\ n = 1, 2.$$

The reactions of sulphenamides with anhydrous HF have also been studied with a view to preparing sulphenyl fluorides, RSF, as a new class of compound.[140] However, on treatment of trichloromethylsulphenyldiethylamine with HF, the following were isolated from the reaction mixture: dichlorofluoromethylsulphenyl chloride, $CFCl_2SCl$, difluorochloromethylsulphenyl chloride, $CF_2ClSCl$, and products derived by cleavage of the S–C bond, namely trichlorofluoromethane and trichloromethylsulphenyl chloride.

$$Cl_3CSNEt_2 \xrightarrow{\text{HF, } -78°\text{C}} CFCl_2SCl + CF_2ClSCl + CCl_3F + CCl_3CSCl.$$

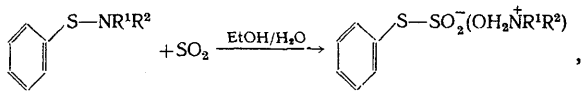
The formation of sulphenyl chlorides in this reaction is evidently a consequence of an initial replacement of chlorine at the carbon atom; the resulting hydrogen chloride then cleaves the S–N bond of the sulphenamide leading to formation of the sulphenyl chloride. Trifluoromethylsulphenyldiethylamine has been used as substrate to prevent this complication. In this case, only cleavage of the S–N bond was noted on heating to 90 °C.

On analysing the mass spectrum of the mixture, an ion of mass 158, corresponding to $CF_3SF_3$, was detected. Thus, in no case is there formation of sulphenyl fluoride on treatment of the corresponding sulphenamide with anhydrous HF.

The ready cleavage of sulphenamides at the S–N bond on treatment with hydrogen halides has been applied both to the removal of *N*-sulphenyl protective groups from amino-acids in peptide synthesis,[128,129,141–143] and to the preparation of certain sulphenyl halides.[122,126,127,130]

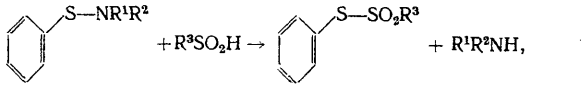
## 4. Reactions with sulphurous acid, sulphinic acids, dialkyl phosphites and monoalkyl phosphinites

Sulphenamides readily react with sulphur dioxide in an aqueous ethanolic medium during 1 h at 60 °C with the formation of Bunte salts in high yield up to 70%.[144]



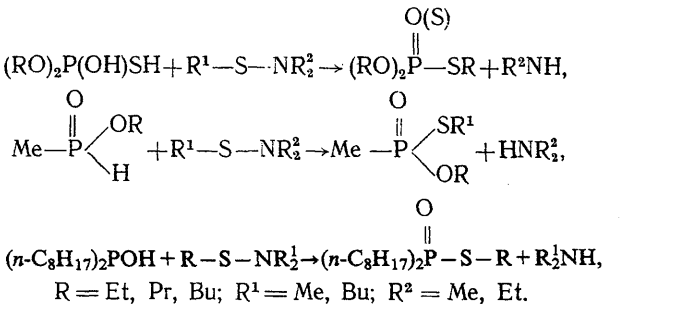
$R^1$ = Me, Et, *iso*-Pr; $R^2$ = Me, Et.

Sulphenamides react in a similar manner with sulphinic acids under the same conditions. In this case thiosulphonic acid esters are obtained.[29,145]



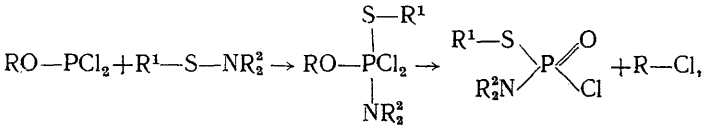
$R^1$, $R^2$ = Alk; $R^3$ = Alk, Ar.

Sulphenamides react with dialkyl phosphites, thiophosphites, phosphinous acid monoesters and dialkylphosphine oxides with the formation of thiolphosphates, thiolphosphonates and thiolphosphinates in 75–95% yield.[146]



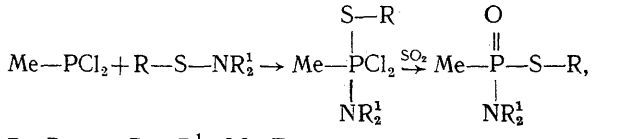
$R$ = Et, Pr, Bu; $R^1$ = Me, Bu; $R^2$ = Me, Et.

Sulphenamides react similarly with phosphonous and phosphorous acid chlorides and with phosphonous anhydrides. For example, *S*-alkyl thiophosphoramidochloridates are obtained by interaction of alkyl phosphorodichloridates with sulphenamides.



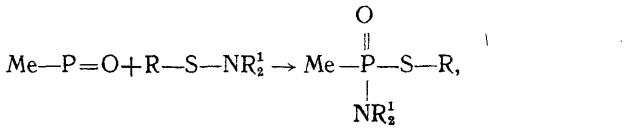
R = Me; $R^1$ = Bu, *tert*-Bu; $R^2$ = Me, Et.

Sulphenamides react with methyldichlorophosphine to afford intermediate phosphoranes which are converted to the corresponding *S*-alkyl thiophosphonamidates on treatment with sulphur dioxide.



R = Bu, *tert*-Bu; $R^1$ = Me, Et.

Methylphosphonous anhydride, like the corresponding dichlorophosphine, also yields *S*-alkyl thiophosphonamidates.



R = Bu, *tert*-Bu; $R^1$ = Me, Et.

## 5. Reactions with hydrogen sulphide and mercaptans

Thio- and dithio-bisamines react comparatively smoothly with hydrogen sulphide to give trisulphides from the former, and polysulphides from the latter.[122]

$$RN_2{-}S_n{-}NR_2 + H_2S \rightarrow H{-}S{-}S_n{-}SH + R_2^2N^+H_2HS_4^-,$$
$$R = Me, Et, iso\text{-}Pr, tert\text{-}Bu;\ n = 1-4.$$

Aryl- and alkyl-sulphenamides react easily with mercaptans to yield the corresponding disulphide and amine, but the same reaction with *N*-acylsulphenamides is less facile. Thus, at room temperature or on cooling, arylsulphenamides are cleaved by mercaptans in dimethylformamide, hexane, or pyridine, thereby providing

disulphides and amines in high yield.[129]

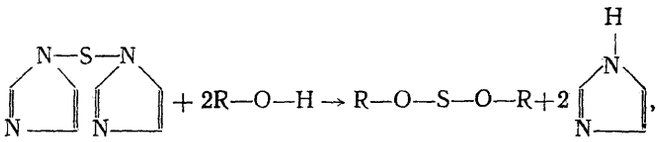
$$R{-}S{-}NR^1R^2 + H{-}S{-}R^3 \xrightarrow{DMF} R{-}S{-}S{-}R^3 + HNR^1R^2,$$

R = Me, Et, Ph, $O_2NC_6H_4$; $R^1$ = Me, Et, Ac; $R^2$ = H, Me, Et; $R^3$ = Et, Pr, Ph.

This procedure is also followed for the removal of sulphenamide protecting groups in peptide synthesis.

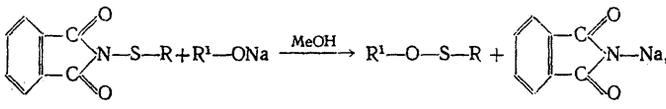
### 6. Reactions with alcohols

Thiobisamines react with alcohols in pentane at low temperature with the formation of sulphoxylic acid esters, as exemplified by the converison of bis(1-imidazolyl) sulphide.[147,148]



R = Et, Bu, *tert*-Bu, *iso*-Pr.

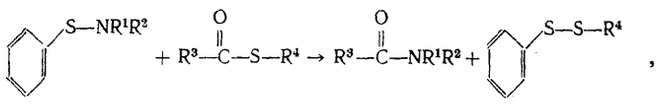
*N*-Acylsulphenamides interact with alkoxides in methanol at 40–50 °C to give the corresponding sulphenic acid esters in 50–70% yield.[149]



R = Bu; $R^1$ = Me, Et, *iso*-Pr, *tert*-Bu.

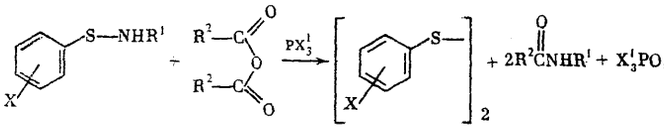
### 7. Reactions with carboxylic acids and their derivatives

Sulphenamides are efficient reagents for the conversion of thiolcarboxylic acid esters, carboxylic acid anhydrides and acyl chlorides to the corresponding amides. Reaction proceeds under mild conditions in the presence of phosphorus(III) compounds, the amide yield sometimes reaching 95%.[150–153]



$R^1$ = Me, Et, Bu, Pr; $R^2$ = Me, Et, Bu, *iso*-Pr; $R^3$ = Me, Et, Bu, Ph; $R^4$ = Ph, $O_2NC_6H_4$.

In the case of carboxylic acid anhydrides, amination of both acyl groups takes place, the phosphorous(III) reagent serving as catalyst and, at the same time, functioning as acceptor of oxygen.[153]

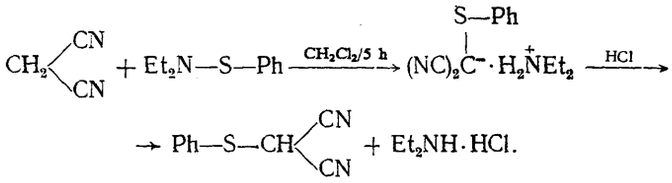


$R^1$ = Ph; $R^2$ = Me, Et, Ph; X = H, $NO_2$; $X^1$ = Ph, OEt.

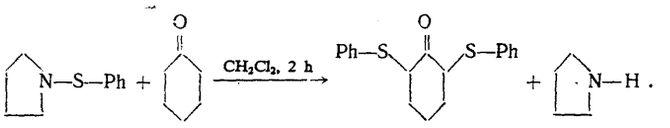
The activating effect of the catalyst is explained by an initial attack on the sulphur atom of the sulphenamide, which ultimately produces an active phosphonium salt. Thus, the catalyst serves to polarise the S–N bond, and consequently effects its cleavage.[152]

### 8. Reactions with CH-acids

Certain sulphenamides have proved effective for the sulphenylation of compounds possessing active methylene groups.[2,154–157] Thus, the diethylammonium salt of phenylthiomalononitrile was isolated in 85% yield by stirring equimolecular amounts of *N,N*-diethylphenylsulphenamide and malononitrile in methylene chloride during 5 h at room temperature.[2] Phenylthiomalononitrile was obtained by treatment of the salt with hydrogen chloride.

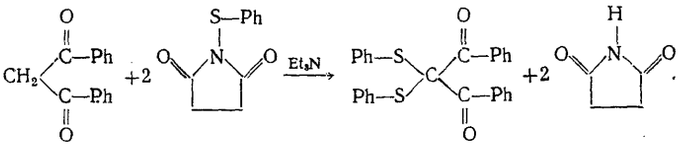


2,6-Bis(phenylthio)cyclohexanone was obtained in high yield by interaction of 2 moles of *N*-phenylthiopyrrolidine with 1 mole of cyclohexanone in methylene chloride at room temperature during 2 h.[2]



It should be pointed out that not every sulphenamide is suitable for sulphenylation. Referring to the above reaction, it is not possible to sulphenylate cyclohexanone by using *N,N*-diethylphenylsulphenamide.

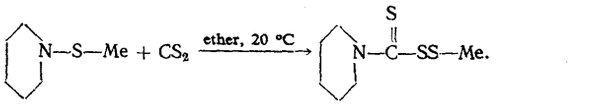
For bis-sulphenylation of methylene groups with *N*-acylsulphenamides, it is recommended that the reaction be conducted in the presence of basic reagents. Thus, bis(phenylthio)dibenzoylmethane was obtained in 50% yield by treatment of 1 mole of dibenzoylmethane with 2 moles of *N*-phenylthiosuccinimide in the presence of 2 moles of triethylamine in methylene chloride at room temperature.[154]



In this case, a succinimide-amine complex is formed together with the triethylammonium salt of the monosulphenylated derivative, which reacts with the sulphenamide to produce bis(phenylthio)-dibenzoylmethane.

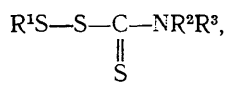
### 9. Addition of sulphenamides to multiple bonds

The reaction of a sulphenamide with carbon disulphide is typical of a sulphenamide addition across a multiple bond, wherein two hetero-functions are incorporated as a result of the familiar S–N bond cleavage. Thus, methyl *N*-cyclopentamethylenetrithiocarbamate was obtained in more than 80% yield by interaction of an ethereal solution of *N*-methylthiopiperidine with carbon disulphide at room temperature over 5 min.[158,159]



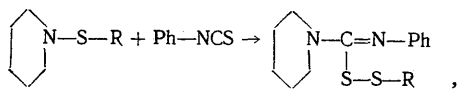
It is suggested that reaction is facilitated by coordination of carbon disulphide to the lone pair on nitrogen, with subsequent insertion into the S–N bond to provide the trithiocarbamate.

However, if the substituent on the sulphur atom of the sulphenamide is strongly electron-accepting, reaction with carbon disulphide does not take place. The following trithiocarbamates have been obtained by this method:



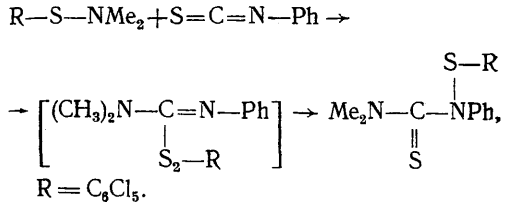
$R^1$ = Me, Et, *tert*-Bu, allyl;
$R^2$ = Me, Et, $(CH_2)_5CH$; $R^1R^2 = (CH_2)_4O$.

Sulphenamides react in the same way with isothiocyanates.[40,160,161] It was found that *S*-alkylthio-*N*-cyclopentamethylene-*N'*-phenylisothioureas are formed by interaction of *N*-*tert*-butylthio- or *N*-ethyl-thio-piperidine with phenyl isothiocyanate as a result of addition across the C=S bond, as takes place with carbon disulphide.



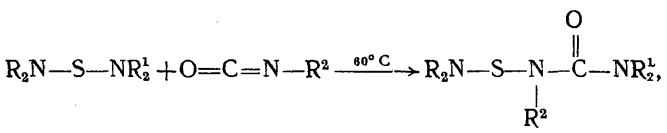
R = Et, *tert*-Bu.

The reaction of sulphenamides with isothiocyanates sometimes leads to the formation of thiourea derivatives rather than *S*-(alkylthio)isothioureas.[160] It would appear that in this case it is the C=N bond of the isothiocyanate which is cleaved, not the C=S bond as in the above case. However, mechanistically this is not true. In fact, in the initial stage of the reaction, the sulphenamide adds across the C=S bond with the formation of the corresponding *S*-(organothio)isothiourea, which subsequently isomerises to the thiourea derivative.



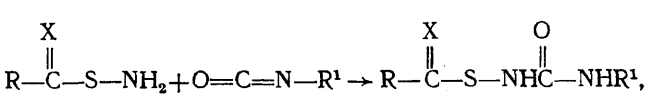
R = $C_6Cl_5$.

Thiobisamines add to isocyanates by cleavage of the C=N bond with the formation of *N*-substituted ureas in 80–90% yield.[160]



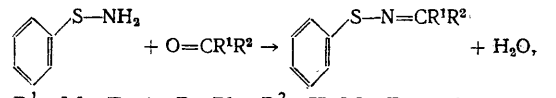
R = Et; $R^1_2 = (CH_2)_5$, $(CH_2)_4O$; $R^2$ = Me, Ph.

*S*-Acylsulphenamides react with isocyanates by addition to the N=C bond, as in the above case. For example, urea derivatives are obtained in 70–80% yield by allowing the reaction mixture to stand in acetone for 20 h.[160]



R = Ph, 3,4-$Cl_2C_6H_3$; $R^1$ = Me, Ph, $ClC_6H_4$; X = O, S.

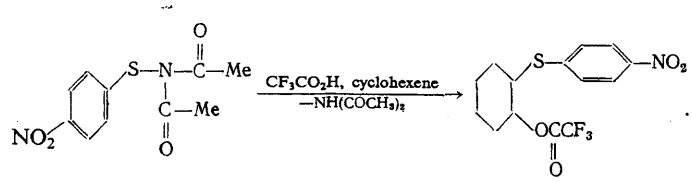
Sulphenamides with a free amino group react with aldehydes and ketones in the same manner as primary amines, affording the corresponding aldimines and ketimines.[162,163]



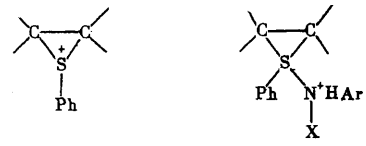
$R^1$ = Me, Et, *iso*-Pr, Ph; $R^2$ = H, Me, Et, *iso*-Pr.

Sulphenamides with a tertiary amino group ($NR_2$) do not react with aldehydes and ketones.

The possibility of adding sulphenamides to a double bond with the participation of an external nucleophile was shown for the first time in 1981, for example, in the reaction of *N*,*N*-diacetyl-*p*-nitrophenylsulphenamide with cyclohexene in the presence of trifluoroacetic acid.[164]

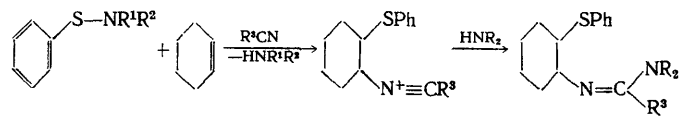


A sulphenium ion is formed as a consequence of two factors: the presence of two electron-accepting acyl groups in the sulphenamide, and the presence of a strong acid in the medium. The ion thus formed adds to the olefin producing an episulphonium complex which is cleaved by the trifluoroacetate ion to provide a *trans*-adduct: *p*-nitrophenyl *trans*-2-(trifluoroacetoxy)cyclohexyl sulphide in the above example. Thus, a sulphenium cation, or an ammonium ion in which the S–N bond is significantly polarised (a partial positive charge developing on the sulphur atom), interacts with the olefin to form either an episulphonium ion (I) or a covalently bonded sulphurane (II), which is subsequently cleaved with the nucleophile.



(I) (II)

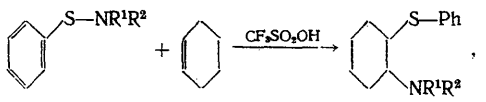
The formation of an episulphonium ion is considered more likely. With a nitrile as the external nucleophile, addition across the multiple bond takes place on activation of the sulphenamides with trifluoromethanesulphonic acid.[165–169] In this way, amidines are obtained in high yield.[165]



R=Me, Et; $R^1$, $R^2$=$(CH_2)_5CH$, $(CH_2)_2O(CH_2)_2$; $R^1$=H; $R^2$=Bu; $R^3$=Ph.

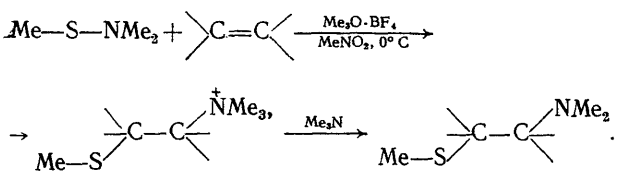
If the reaction of a phenylsulphenamide with cyclohexene in methylene chloride is allowed to proceed in the presence of an external nucleophile as well as trifluoromethanesulphonic acid as

activating agent, then aminosulphides are obtained in high yield.[170–172]

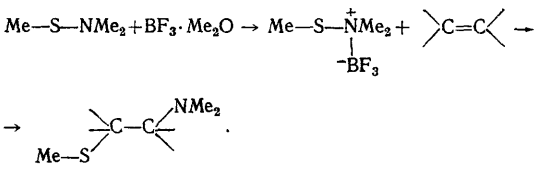


$R^1$, $R^2=(CH_2)_5$, $(CH_2)_2O(CH_2)_2$; $R^1=H$; $R^2=$ *tert*-Bu.

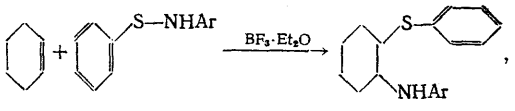
Trimethyloxonium fluoroborate or boron fluoride etherate may also serve as activator. In the presence of the former, sulphenamides interact with olefins in nitromethane to give a β-(methylthio)alkyltrimethylammonium salt which is converted into an amine on treatment with trimethylamine.[173]



In the presence of boron fluoride etherate, reaction of a sulphenamide with an olefin yields a trifluoroboratoammonium salt from which an aminoalkyl sulphide is liberated on treatment with base.

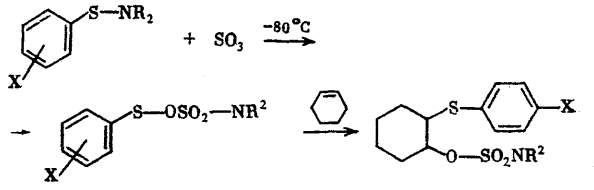


The addition of phenylsulphenamides to cyclohexene in benzene containing a 50% excess of boron fluoride at room temperature leads, stereospecifically, to the corresponding *trans*-adduct in 50 to 90% yield.[174]



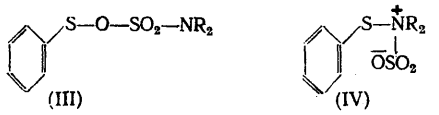
Ar=4-$NO_2C_6H_4$, 4-$ClC_6H_4$, 4-$MeC_6H_4$, 4$MeOC_6H_4$, 3$MeOC_6H_4$.

It has been shown that *N,N*-diethylphenyl- or *N,N*-diethyl-*p*-nitrophenylsulphenamide in the presence of sulphur trioxide also add stereospecifically to cyclohexene, affording *trans*-1,2-disubstituted cyclohexanes in high yield.[175–178]



R = Et; X = H, $NO_2$.

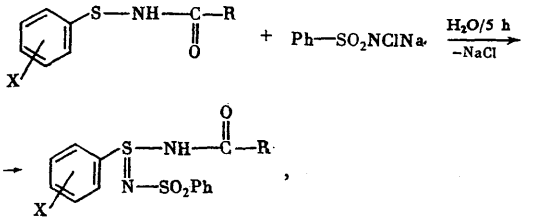
It is proposed that, initially, the sulphenamide and sulphur trioxide form an intermediate, (III) or (IV), from which the electrophilic moiety is derived.[175]



(III) (IV)

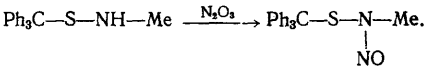
## 10. Other reactions

It has been reported that *N*-acylarylsulphenamides undergo sulphonylimination with sodium *N*-chlorobenzenesulphonamide (Chloramine B). Thus, as with thioethers, Chloramine B interacts with *N*-acylarylsulphenamides in aqueous medium to give the corresponding *N*-acylaryl(sulphonylimido)sulphinamides in 40–80% yield.[179–181]

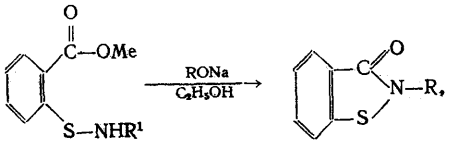


R = Me, Ph; X = H, $NO_2$.

*N*-Monoalkylsulphenamides react with nitrogen oxides ($N_2O_3$) in the same manner as secondary amines to provide nitrososulphenamides in 50–55% yield.[137]

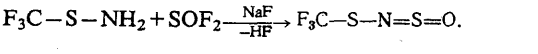


*N*-Monoalkylphenylsulphenamides which possess an *o*-carbalkoxy group cyclise by intramolecular acylation to 1,2-benzoisothiazol-3-ones.[182]

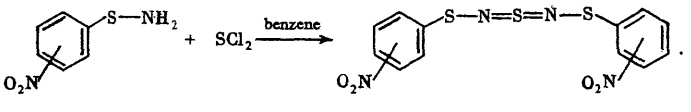


R=Alk; $R^1$=$PhCH_2$, Pr, $CH_2CH_2OH$, Ph, MeOPh.

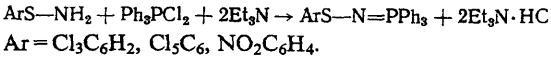
Sulphenamides with a free amino group react with thionyl fluoride, sulphur dichloride and triphenylphosphine dichloride. Thus, in the first case, trifluoromethylthionylimine is obtained by interaction of trifluoromethylsulphenamide with thionyl fluoride in the presence of sodium fluoride at 20 °C.[183]



In the second case, *N,N'*-bis(*p*-nitrobenzenesulphenyl)sulphur diimide is formed in 70% yield by treatment of *p*-nitrobenzenesulphenamide with sulphur dichloride in benzene at room temperature.[184]



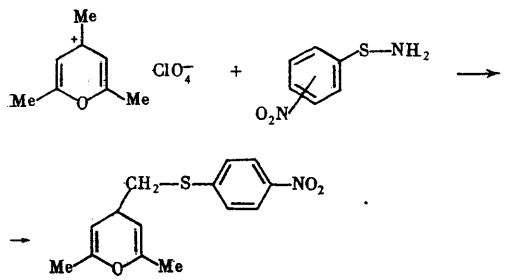
In the third case, boiling a solution of arylsulphenamide and triphenylphosphine dichloride in carbon tetrachloride for 30 min in the presence of tertiary amine affords the corresponding phosphazo compound in 50–90% yield.[185]



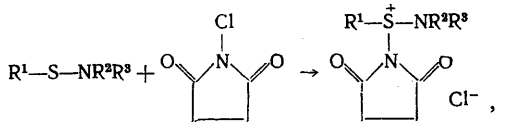
Ar=$Cl_3C_6H_2$, $Cl_5C_6$, $NO_2C_6H_4$.

It has been shown that a thioether is formed in 80% yield by interaction of *p*-nitrobenzenesulphenamide with a 2,4,6-trimethyl-

pyrylium salt which possesses an active methyl group at the 4 position.[185]

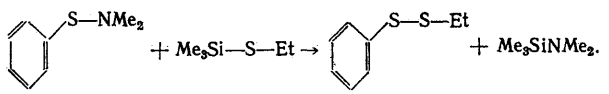


Succinimidosulphonium salts are obtained in 80–90% yield by reaction of sulphenamides with *N*-chlorosuccinimide in methylene chloride at 0 °C.[186]

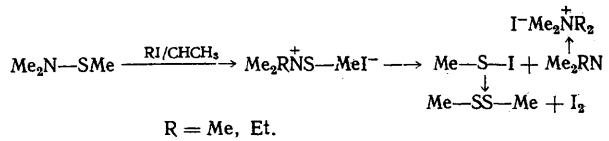


$R^1$ = Me, Et, Ph; $R^2$ = Me, $PhCH_2$; $R^3$ = Me, $PhCH_2$.

It has been reported that unsymmetrical disulphides are obtained by reaction of sulphenamides with alkyl- or aryl-thiosilanes. Thus, ethyl phenyl disulphide was isolated in 47% yield from the reaction of *N,N*-dimethylphenylsulphenamide with ethylthiotrimethylsilane in hexane at 0 °C.[4]

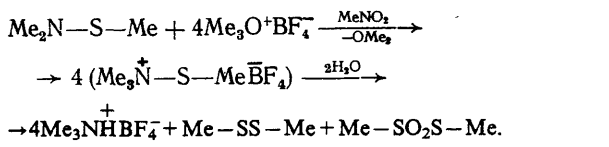


Sulphenamides are alkylated with alkyl iodides with the formation of unstable salts.[4,187–190] Thus, dimethyl disulphide and a tetraalkylammonium iodide were isolated in almost quantitative yield by treatment of *N,N*-dimethylmethanesulphenamide with a solution of methyl or ethyl iodide in chloroform. The reaction proceeds via an unstable alkylthioammonium salt which disproportionates into the disulphide, iodine and the tetraalkylammonium salt.



R = Me, Et.

Furthermore, methylation of sulphenamides with trimethyloxonium fluoroborate in nitromethane also leads to the formation of an alkylthioammonium salt which is very sensitive to moisture and decomposes into the corresponding disulphide, thiosulphonate and trialkylammonium fluoroborate.[190]



A similar reaction takes place on treatment of a thiosulphonium fluoroborate with a tertiary amine in nitromethane.

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