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Progress in the chemistry of sulphilimines

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ABSTRACT. **The information obtained during recent years on the structure, methods of synthesis, and properties of sulphilimines has been correlated.**

The bibliography includes 155 references.

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I. Introduction

The chemistry of sulphilimines or ~~sulphimides~~[1] originated in 1917 after the discovery[2] of the oxidative imination of sulphides, which resulted in a solution to the problem of contamination by mustard gas. Starting from this period the chemistry of sulphilimines has evolved quite rapidly and at the present time is a relatively well-developed branch of organoelemental chemistry.

Convenient preparative methods for obtaining sulphilimines have been developed, their properties have been studied thoroughly, and areas of their practical application have been found.

The interest shown in the chemistry of sulphilimines by many research workers is mainly due to the synthetic importance of these compounds. The lability of the S(IV)=N bond, its ability to be cleaved by both nucleophilic and electrophilic reagents, and also the two active reaction sites (sulphur and nitrogen) provide sulphilimines with the properties of valuable reagents for organic synthesis.

On the other hand, some examples of this class of compounds have the properties of antioxidants of polyolefins[3] and herbicidal, bactericidal, and pharmacological reagents, which also stimulates a particular interest. The chemistry of sulphilimines up to 1976 is covered by several review articles,[1,4,5] one of which[1] is exhaustive. However, since the time of publication of these articles a considerable amount of new information that requires correlating has accumulated, and this has provided the contents of the present review.

II. Nature of the S(V)=N bond and structure of sulphilimines

There is no common view about the nature of the S(IV)=N bond in sulphilimines and in other imino compounds of sulphur, although much attention has been given to this question in the literature.[6–22] This is because the S(IV)=N bond is different from a normal double bond since for elements of the third and subsequent periods of the Periodic Table of chemical elements the overlap of *p*-atomic orbitals (*p*-AOs) is energetically unfavourable. At the same time the structural features positively indicate the multiple nature of this bond but with a low π-order and with a length greater than the corresponding sum of the covalent radii and a high polarity and low potential barrier of internal rotation which does not allow diastereomeric compounds to occur as a result of hindered rotation about the S(IV)=N bond. The lability of the S(IV)=N bond varies over a wide range according to the nature of the substituents on the sulphur and nitrogen atoms. An analysis of these factors and also an analysis of information about the nature of the E=N bond of other organoelemental compounds provided a basis for the assumption that the *d* orbitals of the sulphur atom participate in the formation of the S(IV)=N bond in sulphilimines. This assumption incorporates three basic theories developed during recent years about the nature of the S(IV)=N bond in sulphilimines.

1. The S(IV)=N bond is a normal double bond in which a second bond is formed as a result of overlap between the *p* orbitals of the nitrogen atoms and *d* orbitals of the sulphur atom that have the corresponding symmetry.

2. The S(IV)=N bond is a semipolar bond in which a σ-bond is formed from AOs of *p* type from the sulphur and nitrogen atoms and the second bond is ionic, stabilised through the formation of a charge transfer complex from the electron-rich nitrogen atom (=NR groups) to the sulphur atom with a positively charged R_2S skeleton.

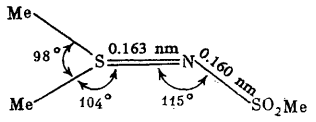
3. The S(IV)=N bond is a double bond in which the π-bond is stabilised through the interaction of the p_π (or *n*) orbitals of the nitrogen atom with the d_π orbitals of the sulphur atom or by a hyperconjugation effect which occurs as a result of the interaction between the unshared electron pair of nitrogen with the electrons of the antibonding σ orbitals of the neighbouring S–C bond ($n_N-\sigma^*_S$ interaction).

A detailed analysis of these three theories about the nature of the S(IV)=N bond, including quantum-mechanical calculations, structural and spectroscopic data, did not lead Egorov[21] to any definite conclusion about the nature of the S(IV)=N bond in sulphilimines. It was stated[21] that sulphilimine molecules $R_2S=NY$ and compounds isoelectronic to them are characterised by a mobile π-electron system, including as an important factor 3*d* orbitals, the population of which increases with an increase in the effective electronegativity of the substituents on the S atom and decreases in the presence of π-electron-acceptor groups on the nitrogen atom. The stabilisation energy of the S(IV)=N bond through $d_\pi-p_\pi$ conjugation is generally small and varies according to the same sequence of change in properties of substituents R and Y. Stabilisation is achieved to a greater extent through the electrostatic interaction between sites with opposite charges—the $R_2\overset{+}{S}$ and $N\overline{Y}$ groups.

On this basis Egorov[21] has proposed that the electronic structure of the S=N bond can be represented as three main resonance structures:

$$S{=}\ddot{N}{-}Y \leftrightarrow \overset{+}{S}{-}\overset{-}{\ddot{N}}{-}Y \leftrightarrow \overset{+}{S}{-}\ddot{N}{-}\overline{Y}.$$

The crystalline and molecular structures of *S*, *S*-dimethyl-*N*-methanesulphenylsulphilimine and certain *N*-arenesulphonylsulphilimines, derived using X-ray diffraction analysis, have been reported in the literature.[6,7,13,15,21] A characteristic feature of these structures is that the tetracovalent sulphur atom together with its surrounding valence bonds forms a trigonal pyramid which is quite stable towards pyramidal inversion, and this is also confirmed by the fact that sulphilimines with suitable substituents can exist in enantiomeric forms caused by the chirality of the sulphur atom. Characteristic bond lengths and bond angles are given below for a typical example of a sulphilimine—*S*,*S*-dimethyl-*N*-methansulphonylsulphilimine



The two C–S(IV) bonds in the molecule of this sulphilimine have different lengths (0.180 nm and 0.178 nm) in the crystalline state, while in solution or the liquid state these bonds are almost equal, which is due to the relatively low rotational barrier of the S(IV)=N bond, the magnitude of which can be assessed from the results of calculations on the hypothetical molecule of $H_2S{=}NH$ (9.60 kcal mol^{-1}).[23] The average length of the S(IV)–C bond is less than the sum of the respective covalent radii (0.183 nm), which is attributed to the possible hyperconjugative type of interaction between the Me groups and the sulphur atom. The bond lengths and bond angles in the molecules of other sulphilimines have very similar values (Table 1). A comparison of the physical parameters of the E=N bond (E = S, Se, Te) of sulphilimines, selenimines,[23] and tellurimines[24] revealed an increase in the length of this bond on going from sulphur to tellurium, which is consistent with the increase in covalent radii of the respective elements.

The frequencies of the stretching vibrations of the S(IV)=N bond (symmetrical and antisymmetrical), according to the literature data,[4,17–19,21] occur over a broad spectroscopic region from 750 to 1400 cm^{-1}, which leads to the assumption that the π-system of the S(IV)=N bond is highly polarisable. It is natural that the high polarisability of the bond is responsible for the considerable dependence of the position of the absorption bands on the nature of the groups on the sulphur and nitrogen atoms, having also a considerable effect on the polarity of the S(IV)=N bond, which varies over a wide range from 1.56 to 10.1 D.[25]

III. Methods for the synthesis of sulphilimines

All methods known at the present time for the synthesis of sulphilimines are based on the use of sulphides and sulphoxides and other tetracovalent sulphur compounds as the initial reactants.

1. Synthesis of sulphilimines from sulphides

a) Oxidative imination of sulphides with *N*-halo compounds

The reactions which are accompanied by the oxidation of an element and formation of an imino group are usually known as oxidative imination.[26] The oxidative imination of sulphides was first discovered by Raper,[2] who showed that mustard gas (β,β′-dichlorodiethyl sulphide) reacts with sodium *N*-chloro-*p*-toluenesulphonamide to form a physiologically inactive compound. It was reported by Nicolet and Willard[27] in 1921 that the product of the reaction between diethyl disulphide and sodium *N*-chloro-*p*-toluenesulphonamide was a colourless crystalline compound. Nicolet and Willard[27] were not able to establish the structure of this compound, and it was only in 1922 that Mann et al.[28] showed that the reaction between disulphides and sodium *N*-chlorosulphonamides results in the formation of sulphilimines.

$$R{-}S{-}R + ArSO_2NNaCl \rightarrow RRS{=}NSO_2Ar + NaCl,$$

$R = Et,\ ClCH_2CH_2;\ Ar\text{-}p\text{-}MeC_6H_4.$

However, not all sulphides are capable of reacting with sodium *N*-chlorosulphonamides to form sulphilimines. It was reported as early as 1922 by Mann and Pope[28,29] that an increase in the number of chlorine atoms in the alkyl groups of the sulphides reduces the capacity of the latter to undergo imination with sodium *N*-chlorosulphonamides. Leandri and Spinelli[30] showed for the reaction between sodium *N*-chloro-*p*-toluenesulphonamide with the bis-sulphides RS–X–Sr (X = Ph, –CH=CH–, $-CH_2-$, $-CH_2-CH_2-$, and others) that both terminal and internal electron-acceptor groups inhibit the process of imination and the *p*-toluenesulphonylimino group introduced as a result of imination of the first sulphur atom inhibits imination of the second sulphur atom. Therefore bis-sulphilimines were only obtained in the case of bis-sulphides in which the sulphur atoms were separated by three or more methylene groups.

Table 1. S(IV)=N bond lengths and angles in sulphilimines $RR^1S{=}NR^2$.

R	R^1	R^2	S=N bond lengths, nm	Bond angles, deg		Refs.
				C–S^{IV}–N	C–S^{IV}–C	
Me	Me	2-$NO_2C_6H_4$	0.1622	106.5 (100.9)*	99.5	[15]
$(-CH_2-)_3$	—	4-$NO_2C_6H_4$	0.1649	—	—	[20]
Me	Me	4-$NO_2C_6H_4$	0.1651	—	—	[20]
Me	Me	$MeSO_2$	0.1627	104.1	98.2	[13]
Me	Me	4-$MeC_6H_4SO_2$	0.1636	102.2	98.4	[13]
Ph	Ph	4-$CH_3C_6H_4SO_2$	0.1628	103.8	101	[21]
Me	Me	PhCO	0.1659	104.2 (99.5)	101	[6]
Me	Me	CCl_2CO	0.1667	104.7 (98.5)	99.9	[22]
Et	Et	$CHCl_2CO$	0.1633	103.8 (99.2)	99.3	[21]

*The second C–S(IV)–N angle is given in brackets.

The effect of the groups on the sulphur atom on the ability of sulphides to undergo imination with sodium *N*-chlorosulphonamides was studied in greater detail by Kucsman et al.[31–34] They established that in the case of the reaction between sulphides and

sodium *N*-chlorosulphonamides in aqueous media that the corresponding sulphoxides are formed together with *N*-arenesulphonylsulphilimines

$$R_2S + ArSO_2NNaCl \xrightarrow{H_2O} \begin{cases} \rightarrow R_2S=NSO_2Ar + NaCl \\ \rightarrow R_2S=O + ArSO_2NH_2 + NaCl \end{cases}$$

In this case the ratio of sulphilimines to sulphoxides depends on the nature of the groups on the sulphur atoms in the initial sulphide, the pH of the reaction medium, and the type of solvent used. In the opinion of Kucsman et al.,[31,32] the ability of sulphides to undergo imination with sodium *N*-chlorosulphonamides is determined by the degree of electron density on the sulphur atom, which should be sufficiently high for the sulphur atom to be able to displace the chloride anion on the nitrogen atom of the *N*-chloroamide, in other words, Kucsman et al. considered that imination of sulphides occurred by nucleophilic substitution and that the formation of sulphoxides was due to the hydrolysis of sulphilimines. They subsequently concluded[35,36] that the imination of sulphides with sodium *N*-chlorosulphonamides was more complex. In their opinion, the sodium *N*-chlorosulphonamide undergoes conversion in an aqueous alcoholic medium as a result of an equilibrium reaction to *N*-chlorosulphonamide (rapidly) and to *N,N*-dichlorosulphonamide (slowly), which are quite reactive electrophilic reagents

$$2ArSO_2NNaCl \overset{H_2O}{\rightleftarrows} 2ArSO_2NHCl + NaOH,$$

$$ArSO_2NHCl \rightleftarrows ArSO_2\bar{N}Cl + H^+,$$

$$ArSO_2NHCl + ArSO_2\bar{N}Cl \rightarrow ArSO_2NCl_2 + ArSO_2\bar{N}H.$$

The formation of *N*-chlorosulphonamides and *N,N*-dichlorosulphonamides was also reported in other studies,[37–39] and the participation of *N,N*-dichlorosulphonamides in this process is supported by their use as iminating agents on reacting with sulphides,[40–43] which, however, is frequently accompanied by other side reactions.

On reacting with *N*-chlorosulphonamides or *N,N*-dichlorosulphonamides, sulphides form a chlorosulphonium cation $R_2\overset{+}{S}Cl$, which reacts with a sulphonamide anion $ArSO_2\bar{N}X$ (X = H, Cl) to form a sulphilimine, while hydrolysis of the chlorosulphonium cation gives a sulphoxide[35,44,45]

$$R_2S + ArSO_2NClX \rightarrow R_2\overset{+}{S}Cl + ArSO_2\bar{N}X,$$

$$R_2\overset{+}{S}Cl \begin{cases} \xrightarrow{ArSO_2\bar{N}X} R_2S{=}NSO_2Ar + XCl \\ \xrightarrow{\bar{O}H} R_2S{=}O + HCl \end{cases}$$

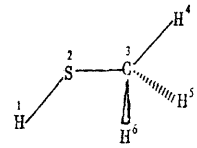
This interpretation of the mechanism for oxidative imination of sulphides with sodium *N*-chlorosulphonamides is consistent with the effect on this process of different factors, namely, the pH of the medium, the type of solvent used, and the nature of the groups on the sulphur atom in the initial sulphide. A low pH of the medium assists the conversion of sodium *N*-chlorosulphonamide to the more active *N*-chloro- and *N,N*-dichloro-sulphonamides but reduces the probability of the existence of the sulphonamide anion. According to the results of Tsujihara et al.[45] in the case of the imination of dialkyl and alkyl aryl sulphides with sodium *N*-chloro-*p*-toluenesulphonamide, a pH of 6 is the most favourable. As solutions of sodium *N*-chlorosulphonamides are alkaline, the addition of a small quantity of acetic acid to the reaction medium increases the yield of sulphilimines.[46–48] Because of the low solubility of sodium *N*-chlorosulphonamides in organic solvents, aqueous solutions of methanol, acetone, dioxan are used as the reaction medium for imination of sulphides as are two-phase media such as water–methylene dichloride, which naturally reduces the yield of sulphilimines and assists the formation of sulphoxides. Yamamoto et al.[49] showed that the use of anhydrous organic solvents such as methylene dichloride as the reaction medium and *N*-chloro-*N*-(dialkylamino)arylsulphonamides, which are readily soluble in these solvents, instead of sodium *N*-chlorosulphonamides, results in the sole formation of sulphilimines in quantitative yield

$$R_2S + R^1(R^2)NN(Cl)SO_2Ar \rightarrow R_2S{=}NSO_2Ar + R^1R^2NCl.$$

When two-phase reaction media are used, phase-transfer catalysts also help to increase the yield of sulphilimines.[50,51]

The susceptibility of the sulphur atom in a sulphide to electrophilic attack by a chlorine cation depends directly on the magnitude of its electron density, which is determined by the nature of the groups on the sulphur atom. Electron-acceptor groups on the sulphur atom in the sulphide hinder imination or make it impossible. Hence, the search for and development of methods for increasing the electron density on the sulphur atom in sulphides is important in terms of theory and synthesis. An analysis of the effective charges on the sulphur atom in the methanethiol molecule and its carbanion, obtained by quantum-mechanical calculations using the CNDO/2 method (Tables 2 and 3) shows[52] that one such method is to form an α-carbanion site in the sulphide molecule.

Table 2. Order of σ bond (*P*) and effective atomic charges (*q*) in the methanethiol molecule.[52]

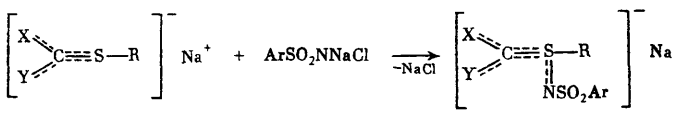


Atom No.	*q*	Bond	*P*
1	−0.011	1–2	0.685
2	−0.043	2–3	0.773
3	−0.059	3–4	0.664
4	0.043	3–5	0.665
5	0.035	3–6	0.665
6	0.035	—	—

A reduction in electron density on the sulphur atom from the effect of electron-acceptor groups in the molecule of the initial sulphide should be balanced in a carbanion by the displacement of charge from the carbanion site.

Koval' et al.[53] demonstrated the basic possibility that arylsulphonylimination of diacylmethyl aryl sulphides containing a mobile α-H atom together with electron-acceptor groups can occur, but the sulphilimines resulting in this case undergo further conversions as a result of imino–ylide tautomerism. The use of their sodium salts instead of these sulphides assists the

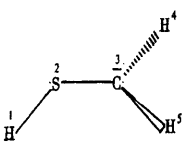
arylsulphonylimination of these compounds in anionic form, as well as the stabilisation of the anion of the resulting *N*-arylsulphonylsulphilimines.[52,54–56]



$R = 2\text{-}NO_2C_6H_4$, $4\text{-}NO_2C_6H_4$, $2,4\text{-}(NO_2)_2C_6H_3$; $X = Y = PhCO$, $X = Y = MeCO$, $X = Y = CN$, $X = Y = EtOCO$;

$X = MeCO$, $Y = EtOCO$.

Table 3. Order of σ bond (*P*) and effective atomic charges (*q*) in the methanethiol carbanion.[52]



Atom No.	*q*	Bond	*P*
1	−0.140	1–2	0.675
2	−0.346	2–3	0.827
3	−0.357	3–4	0.661
4	−0.079	3–5	0.661
5	−0.079	—	—

Other *N*-chloro compounds such as chloramines,[57] *N*-chlorocarboxamides,[58] *N*-chlorourethane,[59] *N*-chloroamidines,[60] *N*-chloroguanidines,[61] and *N*-chlorourea and its derivatives[62,63] react with dialkyl and alkyl aryl sulphides to form aminosulphonium salts, which are converted by bases to the corresponding sulphilimines.

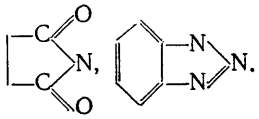
$$R_2S + XNHZ \rightarrow R_2\overset{+}{S}NHZX^- \xrightarrow[-HX]{HB} R_2S{=}NZ,$$

HB – base; X = Cl, Br; Z = H, Alk, Ar, Hetar, AlkCO,

ArCO, EtOCO, R—C(=NR)—, NH_2—N=CH—, NH_2CO.

Sources of chlorine cations are also provided by chlorine,[64] t-butyl hypochlorite,[65–69] sulphuryl chloride,[70] *N*-chlorosuccinimide,[64,71,72] and other heterocyclic *N*-chloro compounds,[64] which react with sulphides at low temperatures to form chlorosulphonium intermediates that are converted by *N*-nucleophiles to sulphilimines.

$$R_2S + Cl{-}Z \rightarrow [R_2\overset{+}{S}{-}Z]\bar{Cl} \rightarrow \xrightarrow{R'NH_2} R_2\overset{+}{S}NHR'\bar{Cl} \xrightarrow[-HCl]{HB} R_2S{=}NR',$$

Z = Cl, t-BuO, SO_2Cl, 

Aliphatic, aromatic, and heterocyclic amines, *N*-aminophthalimide, cyanamide, and sodium sulphonamides and carboxamides are used as *N*-nucleophiles.

b) Oxidative imination of sulphides with hydroxylamine derivatives

The oxidative imination of sulphides with hydroxylaminosulphuric acid, first described by Appel and Buchner,[73,74] is a specific case of the general imination of sulphides with hydroxylamine derivatives and particularly with *N*-arylsulphonyl-*O*-*p*-nitrophenylsulphonylhydroxylamine,[75] *N*-ethoxycarbonyl-*O*-*p*-nitrophenylsulphonylhydroxylamine,[75] and *O*-mesitylsulphonylhydroxylamine.[76,77]

$$R_2S + XNHOY \rightarrow R_2\overset{+}{S}NH(X)\bar{O}Y \xrightarrow[-YOH]{HB} R_2S{=}NX,$$

$X = H$, $ArSO_2$, EtOCO;

$Y = HSO_3$, $2,4,6\text{-}(Me)_3C_6H_2SO_2$, $4\text{-}NO_2C_6H_4SO_2$.

The mechanism of this reaction has not been studied, but it is possible from literature data[26] on the oxidative imination of tertiary phosphines with hydroxylaminosulphuric acid to suggest that there are two mechanisms, one involving the generation of an imene ṄH and the other, more probable, mechanism involving nucleophilic attack by sulphide on the electron-deficient nitrogen atom.

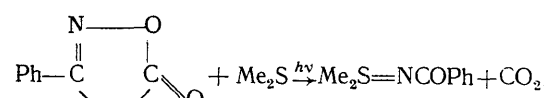
c) Reaction of sulphides with nitrenes

Sulphilimines are formed in good or moderate yield by reaction of sulphides with nitrene generated by photochemical, thermal, and chemical methods. A method involving the photolysis of different organic azides in the presence of an excess of disulphide is the most widely used.

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

X = $ArSO_2$, PhCO, EtOCO, R_2PO and others.

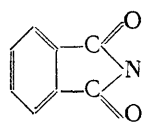
The reaction has been studied in a series of arenesulphonyl,[78] acyl,[79] alkoxycarbonyl,[79] diphenylphosphonyl and dialkylphosphonyl[80] azides. It has been proposed[81] that sulphides react more rapidly with singlet than with triplet nitrenes since the presence in the reaction mixture of products that give rise to the formation of triplet nitrenes inhibits the formation of sulphilimines. The low yields of sulphilimines may be due to their photochemical instability. At the same time during photolysis the sulphilimines themselves are sources of nitrenes, as has been noted[79] in the case of the photolysis of *S,S*-dimethyl-*N*-ethoxycarbonylsulphilimine. Sources of nitrenes are also provided by certain unstable heterocyclic compounds, photolysis of which in the presence of sulphides results in the formation of sulphilimines[82]



The main disadvantage of the method for synthesising sulphilimines by reaction between sulphides and thermally generated nitrenes is the thermal instability of the resulting sulphilimines, which has been observed in the case of the thermolysis of acyl azides,[83] alkoxycarbonyl azides,[83,84] and arylsulphonyl azides[83,85] in the presence of sulphides. It has been shown[86] that in the presence of copper the thermolysis of azides, and hence the reaction between nitrenes and sulphides, occurs at a lower temperature, which helps to increase the yield of sulphilimines.

Chemical generation of nitrenes in order to obtain sulphilimines has been used less often. In the literature there have been reports on only a few sulphilimines by reaction between sulphides and arenesulphonamides[87,88] and *N*-aminophthalimide[1] in the presence of lead tetraacetate

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

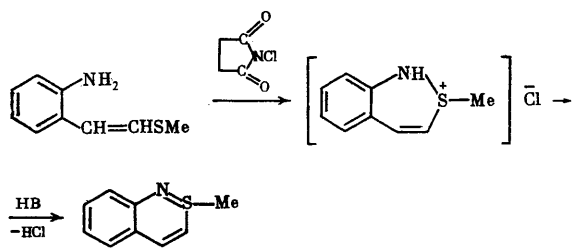
$X = ArSO_2$, 

It cannot be excluded that the formation of sulphilimines in the reaction between sulphides and compounds with an E=N bond (E = S, I), as reported in the literature,[89,90] also occurs via a stage involving generation of nitrenes

$$R_2S + X{=}NTs \rightarrow R_2S{=}NTs,$$
$$X = TsN{=}S,\ ArI$$

d) Oxidative cyclisation of aminosulphides

On treatment with *N*-chlorosuccinimide, aromatic amines containing alkylthio groups at the *ortho*-position form cyclic aminosulphonium salts, which in the presence of bases are converted to cyclic sulphilimines[91,92]



2. Synthesis of sulphilimines from sulphoxides

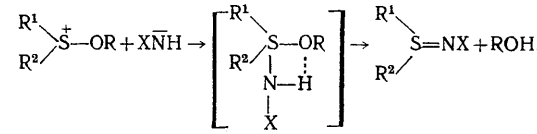
a) Condensation of sulphoxides with amides and amines in the presence of activating electrophilic reagents

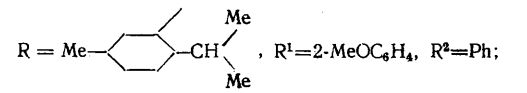
This method involves the generation of active sulphonium salts by the attack of an electrophile on the oxygen atom of a sulphoxide, which is converted to an effective leaving group

$$R_2S{=}O \xrightarrow{E^+} R_2\overset{+}{S}OE \xrightarrow[-HOE,\ -H^+]{R^1NH_2} R_2S{=}NR^1,$$
E – electrophile.

Phosphorus pentoxide,[93] trifluoroacetic anhydride,[93,94] sulphur trioxide, sulphuric acid, and boron trifluoride[95] have been used as activating electrophiles. Amides of sulphonic and carboxylic acids and certain amines have been used as *N*-nucleophiles. A number of sulphilimines have been obtained by the reaction of sodium sulphonamides and carboxamides with alkoxysulphonium salts.[68,96]

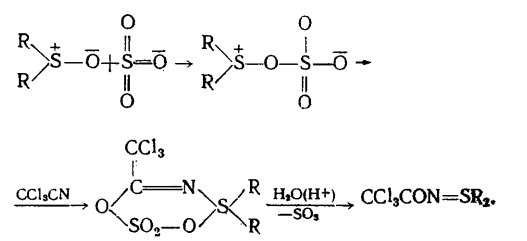
The reaction is stereospecific and occurs with retention of configuration at the sulphur atom, which in the opinion of research workers is due to the formation of an intermediate four-membered cyclic compound which is stabilised by an intramolecular hydrogen bond.





$X = ArSO_2$, CH_2ClCO, $CHCl_2CO$, CCl_3CO, CF_3CO.

The sulphonium salts formed by reaction of sulphoxides with sulphur trioxide react with nitriles to form sulphinylimines.[97] The proposed mechanism of this reaction involves attack by the electron-deficient carbon atom of the nitrile group on one of oxygen atoms of the sulphonium salt, which only takes place for nitriles containing strong electron-acceptor groups:

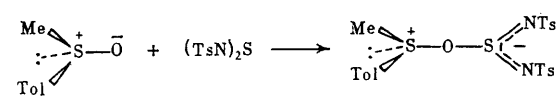


b) Condensation of sulphoxides with *N*-substituted amides

With certain *N*-substituted amides containing groups with polar double bonds as substituents, condensation of sulphoxides takes place in the absence of activating electrophilic reagents.[98–101]

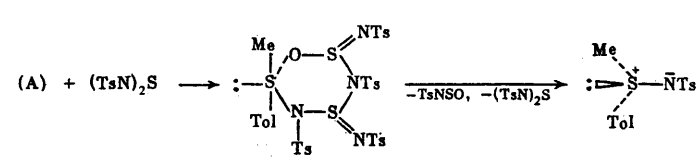
$$R_2S{=}O + YN{=}X \rightarrow R_2S{=}NY + XO,$$
$X = SO,\ CO,\ S{=}NSO_2Ar,\ SCl_2$; $Y = ArSO_2,\ RCO,\ EtOCO,\ Ar$.

The condensation mechanism has been studied in detail in the case of the reaction between methyl *p*-tolyl sulphoxide and *N,N'*-bis(*p*-toluenesulphonyl)sulphurdiimide.[102] It involves attack by the electron-deficient atom of the polar group on to the oxygen of the sulphoxide to form the sulphonium salt (A), whose subsequent conversion is determined by the nature of the solvent.

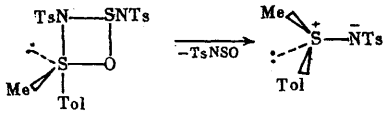


(A)

In pyridine, reaction of the sulphonium salt with a second molecule of sulphurdiimide results in the formation of a six-membered transition state, whose conversion to a sulphilimine is accompanied by inversion of configuration at the chiral sulphur atom.

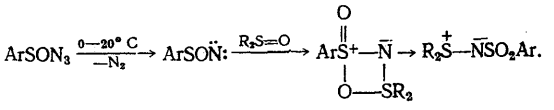


In benzene the reaction takes place via a four-membered transition state with retention of configuration at the sulphur atom.



c) Reaction of sulphoxides with arylsulphinyl azides

In contrast to arylsulphonyl azides, which form *N*-arylsulphonylsulphoximides with sulphoxides,[103] arylsulphinyl azides react with sulphoxides to form *N*-arylsulphonylsulphilimines.[104] It is thought that intermediate arylsulphinylnitrenes react with sulphoxides to form unstable four-membered cyclic compounds that are converted to a sulphilimine:



3. The use of other tetracovalent sulphur compounds in the synthesis of sulphilimines

a) Nucleophilic substitution on a tetracovalent sulphur atom

Nucleophilic substitution of different atoms and groups on a tetracovalent sulphur atom in order to obtain sulphilimines is utilised in two methods. The first of these involves nucleophilic substitution of halogen atoms[105,106] or alkoxy groups[105,107] in order to produce a S(IV)=N bond

$$R_2SX_2 + 3NH_3 \rightarrow R_2S{=}NH + 2NH_4X,$$

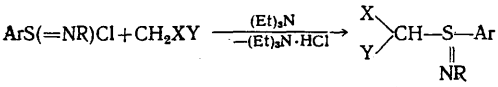
R = Ar, CF_3, X = Cl, F;

$$Ph_2S[OC(CF_3)_2Ph]_2 + RNH_2 \rightarrow Ph_2S{=}NR + 2PhC(CF_3)_2OH,$$

R = H, Alk, Ar, $ArSO_2$.

The second method involves nucleophilic substitution of halogen atoms on the tetracovalent sulphur atom in order to produce an S(IV)–C bond.[108,109]

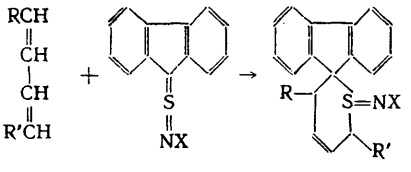
$$F_2SNPh + 2PhLi \rightarrow Ph_2S{=}NPh + 2LiF,$$



R = $(Me)_3C$, $(Me)_2C(CN)$, $ArSO_2$; X = CN, MeCO; Y = CN, MeCO, EtOCO.

b) Reaction between thione-*S*-imines and diene hydrocarbons

It has been shown[110] that *N*-substituted thione-*S*-imines containing arylsulphonyl groups as substituents can perform as active dienophiles in [4 + 2] cycloaddition reactions with conjugated diene hydrocarbons to form sulphilimines containing a sulphur atom in the ring.



R = H, Me; R′ = Me, H; X = *p*-$MeC_6H_4SO_2$.

IV. Reactions of sulphilimines

All of the reactions involving sulphilimines can be divided into three groups, according to the type of change to the S(IV)=N bond: a) reactions that take place without change to the S(IV)=N bond; b) reactions that take place with conversion of the S(IV)=N bond to an S(II)–N or S(IV)–N bond; c) reactions that take place with cleavage of the S(IV)=N bond.

1. Reactions of sulphilimines that take place without change to the S(IV)=N bond

a) Modification of substituents on the sulphur and nitrogen atoms

The directed chemical modification of different substituents on the sulphur and nitrogen atoms in sulphilimines is widely used in the synthesis of new types of these compounds. Particularly convenient in this respect are *S*-haloalkylsulphilimines, which as a result of nucleophilic substitution of the halogen atoms[111] or dehydrohalogenation[112] can readily be converted to new types of sulphilimines.

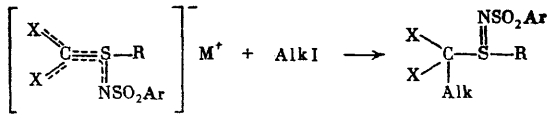
$$ArSO_2N{=}S(Me)CH_2X + RNa \xrightarrow[-NaX]{} ArSO_2N{=}S(Me)CH_2R,$$

X = Cl, Br; R = AlkO, ArO, PhS, NCS;

$$ArSO_2N{=}S(R)CH_2CH_2X \xrightarrow[-HX]{HB} ArSO_2N{=}S(R)CH{=}CH_2,$$

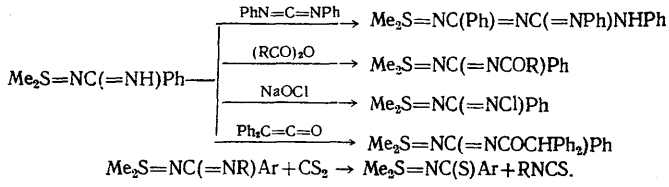
X = Cl, Br; R = Ph, 4-MeC_6H_4.

Replacement of the metal in metal salts of *N*-arylsulphonylsulphilimines by alkyl groups also gives new types of sulphilimines[52,55,56]



X = CN, MeCO, EtOCO; M = Na, Ag; R = 2-$NO_2C_6H_4$, 4-$NO_2C_6H_4$.

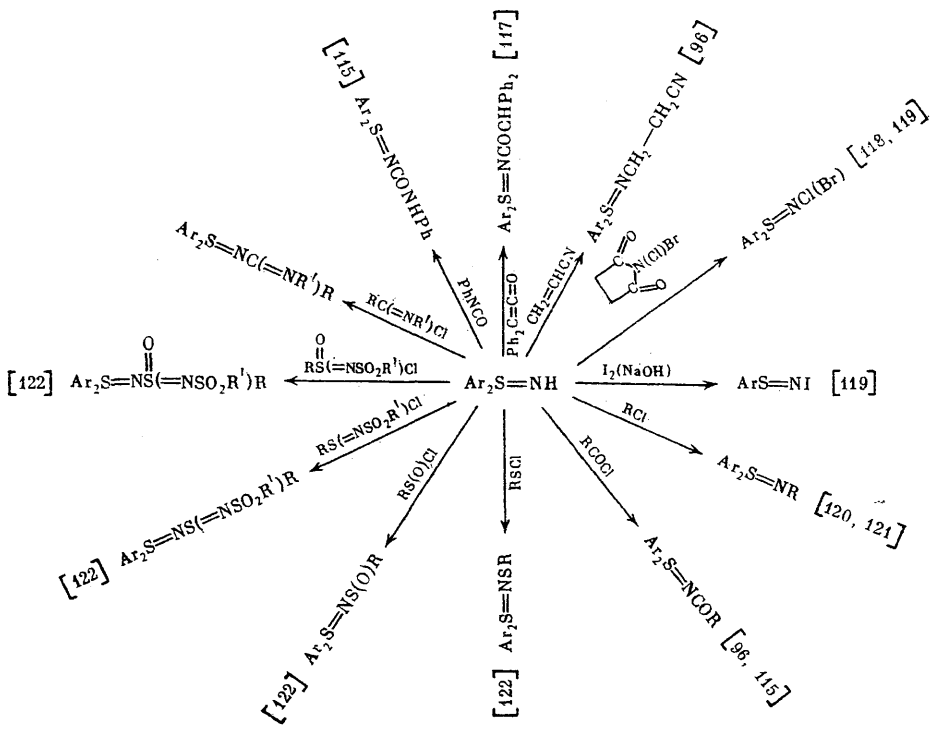
Examples of the modification of groups on the nitrogen atom of *N*-substituted sulphilimines are shown by the reactions of these groups with various reagents, as described in three studies[60,113,114]



$$Me_2S{=}NC(=NR)Ar + CS_2 \rightarrow Me_2S{=}NC(S)Ar + RNCS.$$

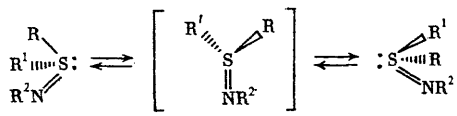
For the synthesis of new types of *N*-substituted sulphilimines, very frequent use is made of sulphilimines that are unsubstituted on the nitrogen atom and which are formed as a result of acid cleavage of

the S(IV)–N bond in *N*-arylsulphonylsulphilimines when they are reacted with 90% sulphuric acid.[115–119]



b) Thermal racemisation of sulphilimines

Sulphilimines with different substituents on the sulphur atom can exist in enantiomeric forms because of the chirality of the sulphur atom. When the temperature is increased interconversion of enantiomers occurs by a pyramidal inversion mechanism via a planar transition state.



Kinetic studies on the thermal racemisation of optically active sulphilimines 2-$MeOC_6H_4S(=NR)Ph$ (R = $PhSO_2$, 4-$MeC_6H_4SO_2$, 4-$MeOC_6H_4SO_2$, MeCO, PhCO, CF_3CO, etc.) which occurs at 75 °C in chloroform showed[123] that together with the known factors for affecting the rate of thermal racemisation (type of solvent, steric factors, etc.) an important part is played by the nature of the groups on the nitrogen atom. Strong electron-acceptor groups on the nitrogen atom reduce the rate of thermal racemisation.

Thus, for example, the rate of thermal racemisation of *N*-tosylsulphilimines is 15 times slower than the rate of thermal racemisation of *N*-trifluoroacetylsulphilimines. In the opinion of Moriyama et al.,[123] this occurs because strong electron-acceptor groups inhibit the $2p-3d$ changes in formation of the S(IV)=N bond in the transition state and also lower the repulsion between the free electron pairs, since they substantially reduce the electron density on the nitrogen atom in the pyramidal geometry of sulphilimines. Therefore, *N*-substituted sulphilimines that contain weak electron-acceptor groups as substituents adopt a configuration that is almost planar. The rate of pyramidal inversion decreases as the absorption frequency of the stretching vibrations due to the S(IV)=N bond decreases in the IR spectra, which is an indication that an increase in the bipolar nature of the S(IV)=N bond increases the barrier of pyramidal inversion.

c) Oxidation of sulphilimines

Sulphilimines are as a rule stable towards oxidation, and they are only oxidised in the presence of strong oxidising agents to form sulphoximides

$$R_2S{=}NR' \xrightarrow{\text{oxidation}} R_2S(=O){=}NR'.$$

R = Alk, Ar; R′ = H, Ar, $ArSO_2$, RCO, ROCO.

The oxidising agents most frequently used are potassium permanganate,[96] hydroperoxides of aromatic carboxylic acids,[115,122] ruthenium tetroxide,[124] hydrogen peroxide in an alkaline medium,[125] and sodium hypochlorite.[126,127] During oxidation in two-phase media, phase-transfer catalysts—Bu_4NX (X = Cl, Br, ClO_4, HSO_4), $PhCH_2N(Et)_3Cl$, $C_{12}H_{15}N(Me)_3Cl$, and others—have been used.[126,127]

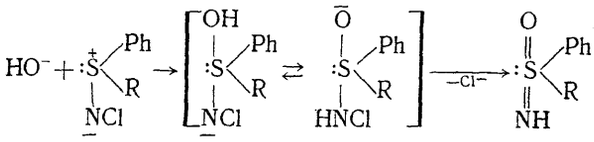
d) Alkaline hydrolysis of sulphilimines

Hydrolytic cleavage of sulphilimines in the presence of mineral acids has been known for a long time and is well studied. As a rule it leads to the corresponding sulphoxides and initial *N*-nucleophiles whatever the structure of the initial sulphilimine. Hydrolysis of sulphilimines in the presence of bases has been insufficiently studied up to now. The composition and structure of the products of this

hydrolysis are frequently determined by different factors and primarily by the structure of the initial sulphilimine. It was reported,[128] for example, that the alkaline hydrolysis of 1-(*N*-*p*-toluenesulphonyl)tetrahydrothiophenesulphilimine in an alcoholic medium results in the formation of 2-alkoxytetrahydrothiophene and *p*-toluenesulphonamide. Alkaline hydrolysis of *N*-chlorosulphilimines in an aqueous medium results in the formation of sulphoximides with an unsubstituted nitrogen atom.[118]

$$R_2S{=}NCl \xrightarrow[-HCl]{H_2O(OH^-)} R_2S(=O){=}NH$$

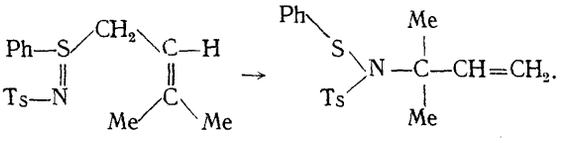
The reaction is stereospecific and in the case of optically active *N*-chlorosulphilimines takes place with 98% retention of configuration at the sulphur atom. The hydrolysis mechanism involves nucleophilic attack by an OH^- group on the sulphur atom to form a transition state which is stabilised through cleavage of a chloride anion.



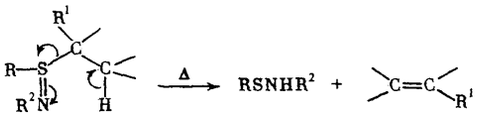
2. Reactions that take place with conversion of the S(IV)=N bond to S(II)–N or S(IV)–N bonds

a) Rearrangement of sulphilimines to sulphenamides

N-Substituted sulphilimines containing an allyl group on the sulphur atom readily undergo various sigmatropic rearrangements, so in many cases they cannot be isolated. One of such types of rearrangement is a [2,3] sigmatropic shift that involves migration of the allyl group from the sulphur atom to the nitrogen atom to form *N*-substituted sulphenamides.[129]



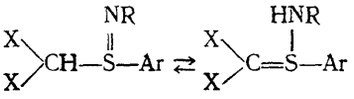
S-Alkylsulphilimines that contain a β-H atom undergo a Pummerer rearrangement on heating, to form sulphenamides and alkenes.[69]



R^1 = H, Me; R^2 = Ar, MeCO.

b) Formation of *S*-aminosulphonium ylides

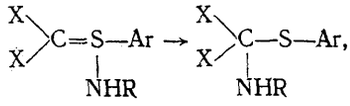
N-Substituted sulphilimines that contain an active α-H atom can undergo a [1,3] sigmatropic rearrangement to form *S*-aminosulphonium ylides



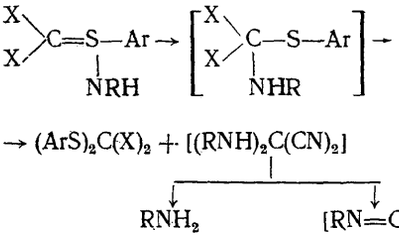
Essentially the rearrangement consists of a prototropic shift in the triad C–S–N, namely an imino–ylide tautomerism, and the possible existence of a given form is determined by the nature of the groups X and R.

In accordance with the principles of an acid-base prototropic equilibrium,[130] a tautomeric equilibrium occurs in those cases where the dissociation constants of both forms differ by a factor of not more than 10^1-10^3. If the difference between the dissociation constants is large, the equilibrium is almost completely displaced towards the form whose dissociation constant is smaller. If we consider with this criterion the C–S–N triad of imino–ylide tautomerism which occurs in a number of *N*-substituted sulphilimines with an active α-H atom, it becomes clear that conversion of the imine form to the ylide form only occurs when the acidity of the CH-form (imine) is comparable to or greater than the acidity of the NH-form (ylide). For the acidity of the CH-form to become equal or greater than the acidity of the NH-form, a strong electron-acceptor effect from groups X is necessary. Therefore, formation of *S*-aminosulphonium ylides was observed[52,53,55,56,109] when strong electron-acceptor groups such as PhCO, MeCO, CN, EtOCO, etc. were introduced as X. In the event that X are weak electron-acceptor groups such as Ph,[131] the prototropic tautomeric equilibrium is completely shifted towards the weakly acidic imine form, namely, a [1,3] sigmatropic rearrangement does not occur.

The stability of *S*-aminosulphonium ylides which are formed as a result of a [1,3] sigmatropic rearrangement of sulphilimines is dependent to a large extent on the nature of groups R on the nitrogen atom. The relatively high stability of *S*-aryl-*S*-(t-butylamino)- and *S*-aryl-*S*-(α-cyanoisopropylamino)sulphonium methylylides has been noted,[109] while *S*-aryl-*S*-(arylsulphonylamino)-sulphonium methylylides[52,53,109] are unstable and undergo further reactions as a result of the migration of the arylsulphonamide group to the carbon atom.



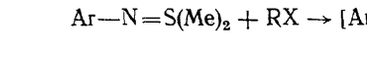
X = PhCO, MeCO; Ar = 4-ClC_6H_4, 2-$NO_2C_6H_4$, 4-$NO_2C_6H_4$;
R = $PhSO_2$, 4-$MeC_6H_4SO_2$;



X = CN, EtOCO; Ar = 4-ClC_6H_4, 2-$NO_2C_6H_4$, 4-$NO_2C_6H_4$;
R = $PhSO_2$, 4-$MeC_6H_4SO_2$.

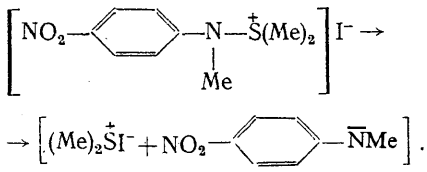
c) Formation of aminosulphonium salts

N-Arylsulphilimines form unstable aminosulphonium salts by reaction with alkylating or acylating agents.[132]

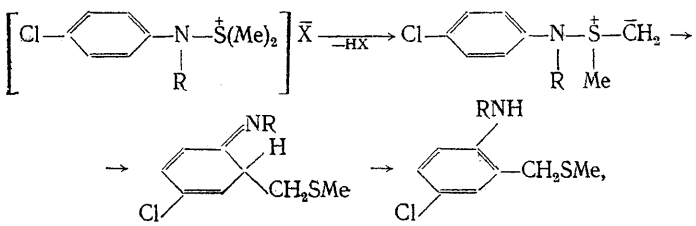


R = Me, X = I; R = EtOCO, X = Cl; R = MeCO, X = $MeCOO^-$;
Ar = *p*-$NO_2C_6H_4$, *p*-ClC_6H_4.

Subsequent conversion of these salts is dependent on the nature of the substituents in the benzene ring of the aryl group and the basicity of X^-. In the case of strong electron-acceptor substituents (such as NO_2) and highly basic X^-, attack by X^- on the positively charged sulphur atom takes place followed by cleavage of the S–N bond



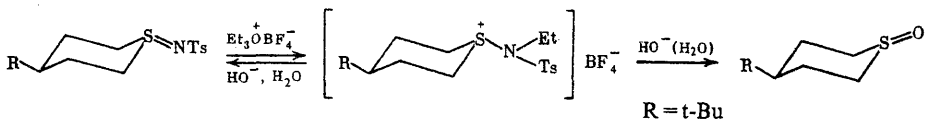
In the case of weak electron-acceptor or electron-donor substituents anion X^- extracts a proton from a MeS group to form an intermediate ylide, which subsequently undergoes an intramolecular sigmatropic rearrangement to give unstable cyclohexadiene derivatives that are converted to more stable benzene derivatives



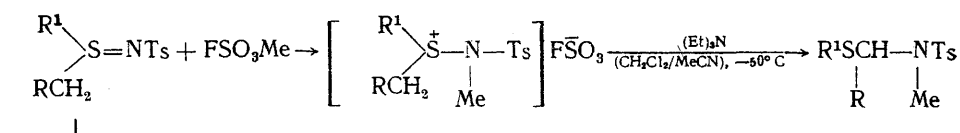
R = Me, X = I; R = MeCO, X = MeCOO; R = EtOCO, X = Cl.

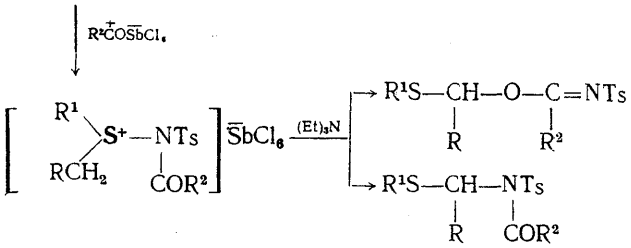
When one of the methyl groups on the sulphur atom is replaced by an ethyl or propyl group, extraction of a proton only occurs from the MeS group, and when it is replaced by a benzyl group the proton is only extracted from the benzyl group, which is correlated with the decrease in acidity in the series $PhCH_2S$ > MeS > $AlkCH_2S$.

N-Arylsulphonylsulphilimines only form aminosulphonium salts in a reaction with highly active acylating and alkylating agents such as oxonium salts ($Et_3\overset{+}{O}BF_4^-$, for example),[129] methyl fluorosulphonate,[133] and complexes of carboxylic acid chlorides with $SbCl_5$.[133] The aminosulphonium salts formed in this case are relatively stable and undergo further reactions only on treatment with mineral or organic bases



R = t-Bu





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

3. Reactions that take place with complete cleavage of the S(IV)=N bond

a) Thermolysis and photolysis of sulphilimines

The composition and nature of the products of thermal decomposition of sulphilimines are determined as a rule by their structure and the conditions of thermolysis. At the same time the thermal destruction processes are often accompanied by various rearrangements, which also contributes to the variety of thermolysis products. This, for example, thermolysis of *N*-acyl-*S*,*S*-diphenylsulphilimines[134] is accompanied by a Curtius rearrangement with the formation of sulphides and isocyanates

$$Ph_2SNCOR \xrightarrow{200\ ^\circ C,\ 2\ h} RNCO + Ph_2S,$$
$$R = PhCH_2,\ PhCH_2CH_2,\ 2,4,6\text{-}(Me)_3C_6H_2,\ Ph.$$

Thermolysis of *N*-*p*-toluenesulphonyl-*S*,*S*-dimethyl- and -diphenylsulphilimines[135] at 300 °C in a current of nitrogen is accompanied by reduction reactions to form mixtures of products, from which Me_2S, $(MeS-)_2$, $(MeS-)_2CH_2$, $4\text{-}MeC_6H_4SO_2NH_2$, PhMe, $(4\text{-}MeC_6H_4S-)_2$, and $4\text{-}MeC_6H_4SSMe$ are isolated. Thermolysis of heterocyclic sulphilimines is often accompanied by ring expansion.[136] The primary products of the photolysis of sulphilimines[137,138] as a rule are the initial sulphides and nitrenes, which, depending on their structure and the type of reaction medium, form various secondary products.

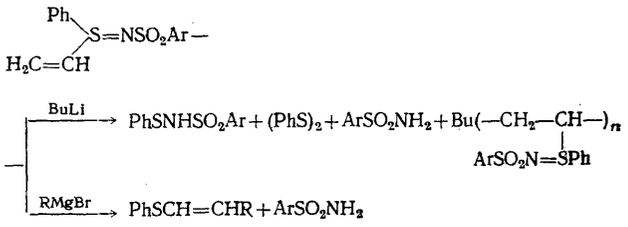
b) Reduction of sulphilimines

Sulphilimines are readily reduced by various reducing agents to give the initial sulphides

$$RR^1S{=}NR^2 \xrightarrow{\text{(reduction)}} RSR^1 + R^2NH_2,$$
$$R = R^1 = Alk,\ Ar;\ R^2 = H,\ Ar,\ AlkSO_2,\ ArSO_2.$$

Phosphorus pentasulphide,[117] titanium tetrachloride with metallic zinc,[121] cysteine,[139] sodium iodide,[140] lithium aluminium hydride,[141] and others have been used as reducing agents. The reaction of *N*-arylsulphonyl-*S*-aryl-*S*-vinylsulphilimines with organolithium and

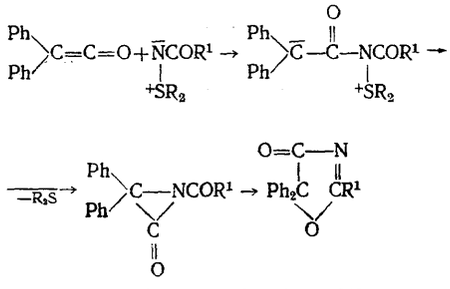
organomagnesium compounds is accompanied by reduction of these sulphilimines[142]



c) Cycloaddition reactions

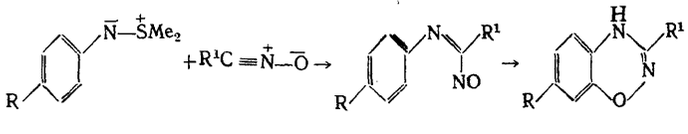
Because of the ylide nature of the S(IV)N=N bond in sulphilimines, they can be used in cycloaddition reactions with compounds containing active double or triple bonds and also systems of cumulated and conjugated double bonds. Meth-Cohn et al.[143] have studied the [4 + 2] cycloaddition of *N*-substituted sulphilimines with compounds containing active C=C bonds. The resulting adducts undergo cleavage to form the highly reactive sulphenylamines R–N=S (R = PhCO, EtOCO, $ArSO_2$). Adducts of the [2 + 2] cycloaddition of sulphilimines to carbon disulphide[114,132] are cleaved to form isothiocyanates, sulphides, and sulphur. Certain cycloaddition reactions only involve the nitrogen atom and groups bonded to it. These reactions are used in the synthesis of heterocyclic compounds. One such reaction is the interaction of *N*-acylsulphilimines with diphenylketene.[144]

The first step in this reaction is nucleophilic attack by the nitrogen atom of the sulphilimine on the electron-deficient carbon atom of the C=O group in diphenylketene followed by cyclisation of the intermediate bipolar compound to form an unstable ethylenimine derivative, which is converted to a more stable 1,3-oxazolin-4-one derivative.

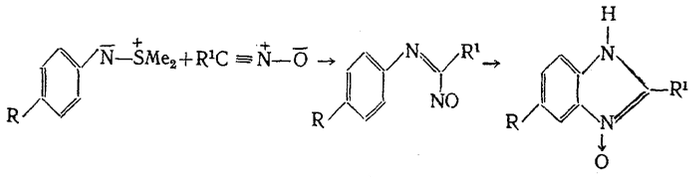


R = Me, Ph; R^1 = Me, CF_3, Ph, $PhCH_2$.

Gilchrist et al.[145] reported that the reactions products from cycloaddition of *N*-arylsulphilimines with nitrile oxides are 1,2,4-benzoxadiazines

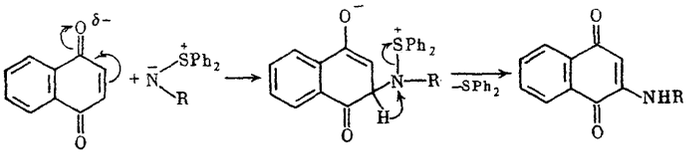


However, according to the results of Shinsaku et al.,[146] cycloaddition does not involve the oxygen atom but the nitrogen atom of the oxynitrile to form benzimidazole *N*-oxides

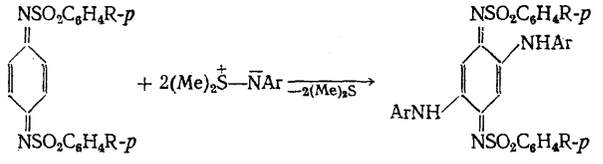


d) Addition to quinoid systems

The high nucleophilicity of nitrogen in *N*-arylsulphilimines can be utilised in their nucleophilic addition reactions to the carbon atoms of a polar system of conjugated bonds of quinones[147] and quinonimines.[148] The proposed mechanism for addition involves nucleophilic attack by the nitrogen atom of the sulphilimine on the terminal carbon atom of the conjugated system of bonds to give an unstable betaine, which is converted as a result of displacement of the sulphonium group by a proton to more stable quinone and quinonimine derivatives.



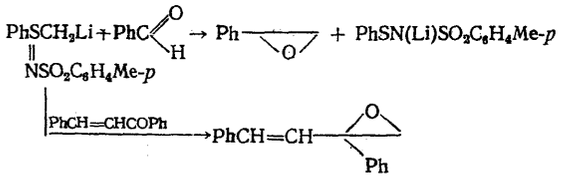
R = $PhCH_2$



R = H, Me; Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-$NO_2C_6H_4$.

e) Transfer of alkylidene groups of *N*-arylsulphonylsulphilimines

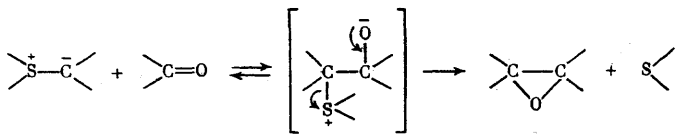
The strong electron-acceptor effect of the arylsulphonylimino group increases the acidity of the α-H atoms of the *S*-alkyl groups, which assists their replacement by an alkali metal atom. Organometallic compounds of this type are used as nucleophilic reagents that transfer alkylidene groups to an electrophilic double bond (such as C=O), forming a three-membered ring.[149] The leaving group whose separation results in the formation of the three-membered ring is a stable *N*-arylsulphonylsulphenamide anion, which also assists this process



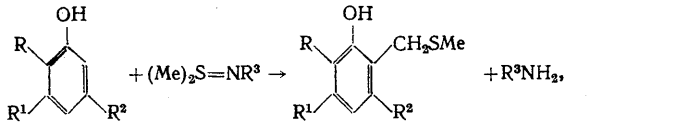
This reaction is characterised by its high stereoselectivity and when other *S*-alkylsulphilimines are used, the resulting 1,2-disubstituted oxiranes mainly have a *trans* structure.[150]

By analogy with the mechanism for transfer of the alkylidene group of sulphur ylides to an electrophilic double bond,[139] the mechanism of this reaction involves the formation of an intermediate

betaine followed by cyclisation through direct substitution at the carbon atom.

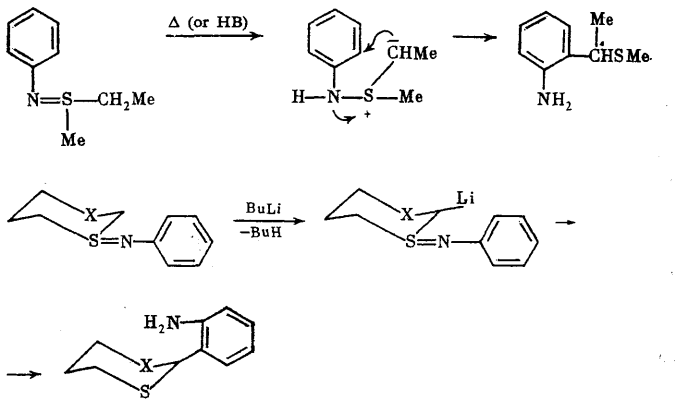


The use of *S,S*-dimethylsulphilimines for the introduction of a methylthiomethylene group into the aromatic ring of phenols has been reported in the literature.[151]



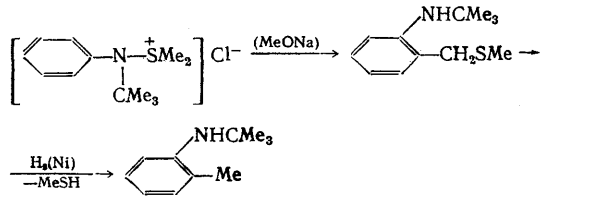
R = Me, OMe; R^1 = H, Me; R^2 = H, Me; R^3 = $ArSO_2$; 2,4-$(NO_2)_2C_6H_3$.

On heating[152] and also by treatment with bases[153] or organolithium compounds,[154] certain *N*-arylsulphilimines undergo a type of Sommelet reaction



X = CH_2S.

Gassman et al.[155] utilised a similar rearrangement of aminosulphonium salts for the *ortho*-alkylation of arylamines.



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