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ADVANCES IN THE CHEMISTRY OF SULFIMIDES AND RELATED COMPOUNDS

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The present review deals with the chemistry of sulfimides and related compounds. Some problems concerning the nature of the S=N bond, methods of synthesis, spectral and chemical properties of sulfimides and iminosulfinic acid derivatives (chlorides, amides, esters) are considered.

Key words: Oxidative imination, oxidative halogenation, oxidative amidation, oxidative alkoxylation, sulfimides, iminosulfinic acid derivatives

CONTENTS

1. INTRODUCTION

Sulfimides (or sulfilimines) are compounds with the general structure $R^1R^2S = NR^3$ (R^1 = Alk, Ar, Het; R^2 = Alk, Ar, Het; R^3 = H, Cl, Br, Alk, Het, $ArSO_2$, ArCO etc.). The compounds most closely related to sulfimides are the derivatives of iminosulfinic or imidosulfinic acids normally formed when one of the substituents at the sulfimide sulfur atom is a halogen atom (iminosulfinic acid halides), an amido group (iminosulfinic acid amides) or an alkoxy group (iminosulfinic acid esters).

The chemistry of sulfimides and related compounds dates back to 1917 when oxidative imination was discovered as a means to solve the problem of yperite decontamination.[1] Since that time the chemistry of these compounds has been developed rather actively and at present it represents a comparatively advanced branch of sulfurorganic chemistry. Appropriate methods to obtain these compounds have been developed, their properties have been studied comprehensively, and practical applications have been found for these compounds.

The interest displayed by many researchers in the chemistry of sulfimides and related compounds is, first of all, due to its synthetic importance. The lability of the S=N bond, its ability to cleave under the action of both nucleophilic and electrophilic reagents as well as the presence of two reaction centers (sulfur and nitrogen) make these compounds useful synthons. On the other hand, some representatives of this group of compounds are useful as polyolefin antioxidants,[2,3] pesticides,[4-8] bactericides,[9-11] and pharmaceutical[12-14] preparations, electrolytic additives,[15,16] and as sensitizers of water photolysis[17] which is of some interest as well.

A number of reviews on certain aspects of the chemistry of sulfimides[18-20] and iminosulfinic acid derivatives[21,22] have been published. However, the most comprehensive review[20] is now approximately ten years old. The present review is intended to supplement and update this information.

2. SYNTHESIS

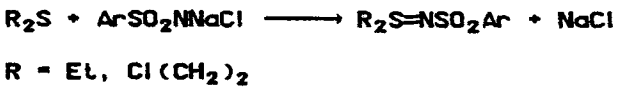
2.1. *Synthesis of Sulfimides*

All presently known methods for the synthesis of sulfimides are based on sulfides and sulfoxides as well as another tetracoordinate sulfur compounds as starting materials.

2.1.1. *Synthesis of Sulfimides from Sulfides*

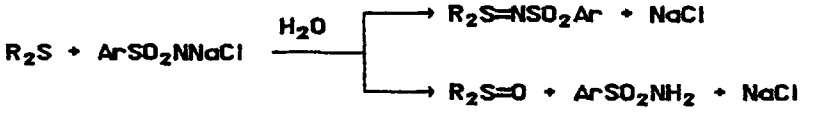
2.1.1.1. *Oxidative Imination of Sulfides with* N-*Halo Compounds* It is customary to call conversions accompanied by element oxidation and imino group formation oxidative imination.[21] Sulfide oxidative imination was first discovered by

Raper who showed that yperite (β,β′-dichlorodiethyl sulfide) when reacting with chloramine-T forms a physiologically inactive substance. Further it has been reported[23] that the product of the reaction of diethyl sulfide with the same reagent was a colorless crystalline substance. The authors failed to determine its structure and it was not until 1922 that Mann *et al.*[24] showed that the reaction of sulfides with *N*-chloroarenesulfonamide salts produced sulfimides (Scheme 1).



Scheme 1

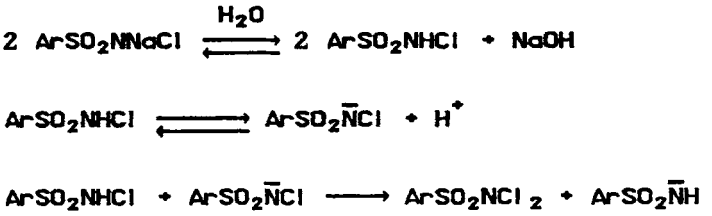
Not all sulfides, however, can react with *N*-chloroarenesulfonamide salts to yield sulfimides. Mann *et al.*[24,25] noted that an increase in the number of chlorine atoms in the alkyl groups of the sulfide reduces the ability of the latter to become iminated by *N*-chloroarenesulfonamide salts. Using as an example the reaction of chloramine-T with bis-sulfides RS—X—SR (X = C_6H_4, CH=CH, CH_2, CH_2—CH_2, etc.) the authors[26] showed that electron acceptor groups, both terminal and internal, hinder the imination and that the *p*-toluenesulfonylimino group introduced at the first sulfur atom hinders the imination of the second sulfur atom. Therefore, bis-sulfimides were obtained only with bis-sulfides in which the sulfur atoms are separated by three or more methylene groups. A more detailed study of the effect of the nature of the substituents at the sulfur atom upon the ability of sulfides to become iminated by *N*-chloroarenesulfonamide salts is presented in papers by Kucsman *et al.*[27–30] These authors established that in the reaction of sulfides with *N*-chloroarenesulfonamide salts in water the corresponding sulfoxides are formed together with *N*-arenesulfonyl sulfimides (Scheme 2).



Scheme 2

In this case the ratio of sulfimide to sulfoxide depends on the nature of substituents in the sulfide, the pH of the reaction medium, and the solvent type. In the authors' opinion[27,28] reactivity of sulfides towards *N*-chloroarenesulfonamide salts requires an electron density at the sulfur atom which must be sufficient for the displacement of the incipient chloride anion by the sulfur atom, *i.e.*, these authors think that the oxidative imination of sulfides involves a nucleophilic displacement mechanism and that the sulfoxide is formed by hydrolysis of the sulfimide. Later on, the same group[31,32] came to the conclusion that sulfide imination with *N*-chloroarenesulfonamide salts is more complicated. In an aqueous-

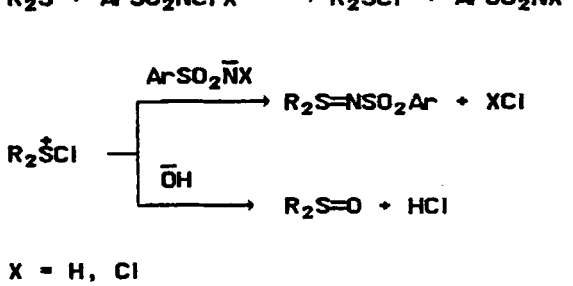
alcoholic medium the *N*-chloroarenesulfonamide salts is transformed, in an equilibrium reaction, to *N*-chloramide (fast) and *N,N*-dichloramide (slow) which are rather reactive electrophilic reagents (Scheme 3).



Scheme 3

The formation of *N*-chloroarenesulfonamides and *N*-dichloroarenesulfonamides from *N*-chloroarenesulfonamide salts has also been mentioned in other papers[33-35] and the involvement of *N,N*-dichloroarenesulfonamides in this reaction is supported by their application as iminating agents in the reaction with sulfides[36-39] which, however, is often accompanied by side reactions.

Upon reaction with *N*-chloroarenesulfonamides or *N,N*-dichloroarenesulfonamides a sulfide forms a chlorosulfonium cation $R_2\overset{+}{S}Cl$ which reacts further with the sulfonamide anion $ArSO_2\bar{N}X$ (X = H, Cl) to form a sulfimide, whereas hydrolysis of the chlorosulfonium cation leads to a sulfoxide[31,40,41] (Scheme 4).



Scheme 4

This interpretation is in good agreement with the effect of various factors on this process, namely, pH solvent and the nature of the substituents in the starting sulfide. A low pH of the medium favors the conversion of *N*-chloroarenesulfonamide salts to the more active *N*-chloro- and *N,N*-dichloroarenesulfonamides, but decreases the concentration of the sulfonamide anion. In the opinion of the authors,[41] in the case of the imination of dialkyl and alkyl aryl sulfides with chloramine-T, pH 6 is the optimum.

Solutions of *N*-chloroarenesulfonamide salts being alkaline, the addition of a small amount of acetic acid to the reaction medium increases the yield of the

sulfimide.[42-44] Because of the poor solubility of *N*-chloroarenesulfonamide salts in organic solvents use is made of aqueous methanol, acetone, or dioxane as well as of two-phase media, *e.g.* water-methylene chloride which, however, decreases the sulfimide yield and favors the formation of sulfoxide. As shown,[45] use of water-free organic solvents, *e.g.* methylene chloride, and of *N*-chloro-*N*-(*N'*,*N'*-dialkylamino)arenesulfonamides (which are readily soluble in such solvents) instead of *N*-chloroarenesulfonamide salts, brings about the selective formation of sulfimides in quantitative yield (Scheme 5).

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

$R = (CH_2)_4$, $PhCH_2$, Ph, $4\text{-}MeC_6H_4$, $4\text{-}ClC_6H_4$;

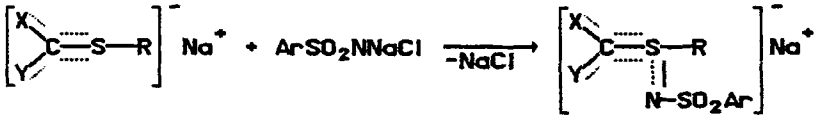
R^1 = Me, Bu; R^2 = Me, Bu, Ph, CH_2

Scheme 5

In two-phase reaction media the formation of the sulfimide is also favored by phase-transfer catalysts.[46,47]

The susceptibility of sulfide sulfur to electrophilic attack by a chlorine cation is directly related to its electron density which is governed by the substituents of the sulfide. In this connection methods to increase the electron density on the sulfur atom in sulfides are theoretically and synthetically important. The analysis of the effective charge on the sulfur atom of methanethiol and its C-anion obtained by CNDO/2 quantum mechanical calculations shows[48] that one such method is the creation of an α-C-anionic center in the sulfide molecule. A decrease in the electron density on the sulfide sulfur of the starting sulfide is compensated in the C-anion at the expense of the electron displacement from the carbanionic center.

It has been shown[49] that (diacyl)methyl aryl sulfides containing, along with electron acceptor groups, a mobile α-H-atom can be arenesulfonyliminated, although the sulfimides formed in this case undergo further transformations due to their imino ylide tautomerism. Use of the sodium salts instead the present sulfides facilitates the arenesulfonylimination of these compounds in the anion form and the stabilization of the anion of the *N*-arylsulfonyl sulfimides formed (Scheme 6).[48,51-53]

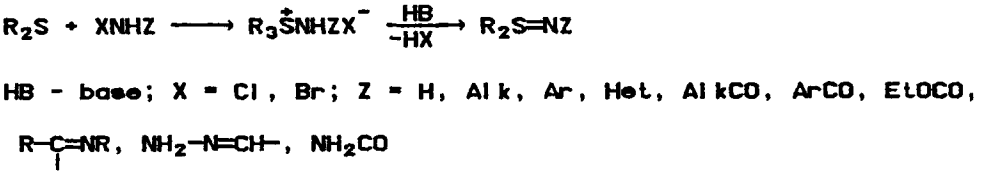


R = $2\text{-}NO_2C_6H_4$, $4\text{-}NO_2C_6H_4$, $2,4\text{-}(NO_2)_2C_6H_3$; X = Y = PhCO,

X = Y = MeCO, X = Y = CN, X = Y = EtOCO; X = MeCO, Y = EtCO

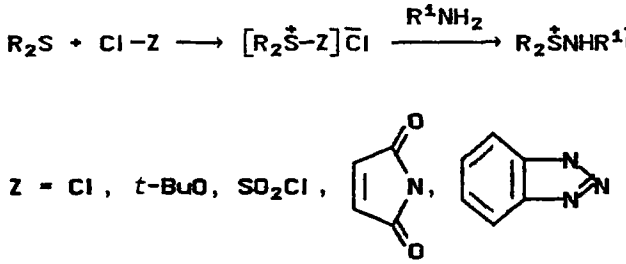
Scheme 6

Other *N*-chloro compounds such as chloramines,[54] *N*-chlorocarboxamides, *N*-chlorourethane,[56] *N*-chloramidines,[57] *N*-chloroguanidines,[58] *N*-chlorourea and its derivatives[59,60] form with dialkyl and alkyl aryl sulfides aminosulfonium salts which are converted by base to the corresponding sulfimides (Scheme 7).



Scheme 7

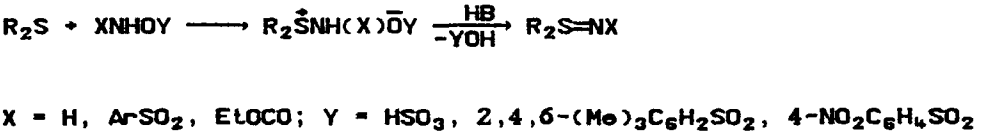
For the chlorination use can also be made of chlorine,[61] *t*-butyl hypochlorite,[62–66] sulfuryl chloride,[67] *N*-chlorosuccinimide,[68,69] and other heterocyclic *N*-chloro compounds[61] which, when reacting with sulfides at low temperatures, form chlorosulfonium intermediates which are converted to sulfimides by the action of N-nucleophiles (Scheme 8).



Scheme 8

Aliphatic, aromatic and heterocyclic amines, *N*-aminophthalimide, cyanamide, and sodio amides of sulfonic and carboxylic acids are used as N-nucleophiles.

2.1.1.2. *Oxidative Imination of Sulfides with Hydroxylamine Derivatives* The oxidative imination of sulfides by hydroxylaminosulfuric acid, described in[70,71] for the first time, is a particular case of the general reaction of sulfide imination with hydroxylamine derivatives and, in particular, with *N*-arylsulfonyl-*O*-(*p*-nitrophenylsulfonyl)hydroxylamine,[72] *N*-(ethoxycarbonyl)-*O*-(*p*-nitrophenylsulfonyl)hydroxylamine,[72] and *O*-(mesitylsulfonyl)hydroxylamine[73,74] (Scheme 9).



Scheme 9

The mechanism of this reaction has not been investigated; nevertheless, relying upon the literature data[75] on the oxidative imination of tertiary phosphines with hydroxylaminosulfuric acid two versions of a mechanism may be suggested: the first one, involving generation of imene (N̈H) and the second, more probable version, involving nucleophilic attack of the sulfide on the electron-deficient nitrogen atom.

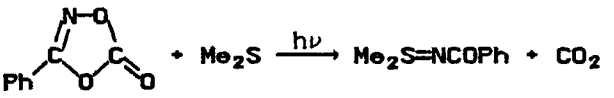
2.1.1.3. *Reaction of Sulfides with Nitrenes* Sulfimides are formed in good to moderate yield by the reaction of sulfides with nitrenes generated by photochemical, thermal or chemical methods. The most widely applied method includes the photolysis of various organic azides in the presence of excess sulfide (Scheme 10).

$$XN_3 \xrightarrow{h\nu} :\ddot{N}X \xrightarrow{R_2S} R_2S{=}NX$$

$$X = ArSO_2,\ PhCO,\ EtOCO,\ R_2PO$$

Scheme 10

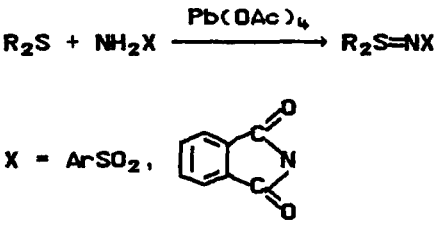
The reaction has been studied with arenesulfonyl,[76] acyl,[77] alkoxycarbonyl,[77] diphenylphosphonyl, and dialkoxyphosphonyl azides.[78] It is expected[79] that sulfides react most likely with singlet nitrenes rather than with triplet ones since the presence, in the reaction mixture, of substances causing the formation of triplet nitrenes inhibits the formation of sulfimides. The photochemical instability of sulfimides may be the cause of the low yields. Under photolytic conditions sulfimides themselves are the source of nitrenes as noted[77] in the case of the photolysis of *S*,*S*-dimethyl-*N*-(ethoxycarbonyl) sulfimide. Another nitrene source are some unstable heterocyclic compounds, the photolysis of which in the presence of sulfides brings about the formation of sulfimides (Scheme 11).[80]



Scheme 11

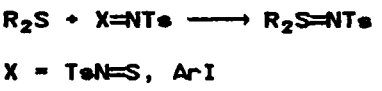
The principal shortcoming of the synthesis of sulfimide by reaction of sulfides with thermally generated nitrenes is the thermal instability of the sulfimides formed as noted in the thermolysis of acyl azides,[81] alkoxycarbonyl azides,[81,82] and arylsulfonyl azides[81,83] in the presence of sulfides. In the presence of copper,[84] azide thermolysis and hence the reaction of nitrenes with sulfides proceeds at a lower temperature, thus increasing the yield of sulfimide.

Chemical generation of nitrenes for the preparation of sulfimides is used more rarely. The synthesis of only a few sulfimides by the reaction of sulfides with arenesulfonamides[85,86] and *N*-aminophthalimide[18] in the presence of lead tetraacetate has been described (Scheme 12).



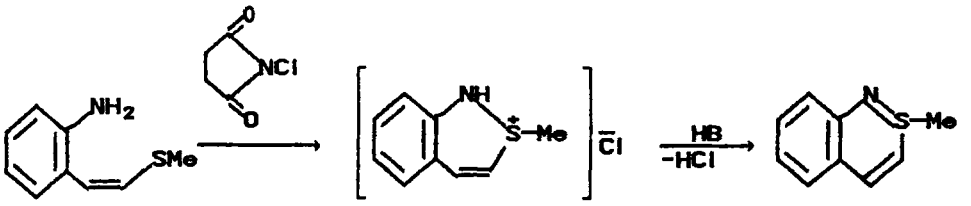
Scheme 12

It is also possible that the formation of sulfimides in the reaction of sulfides with E=N (E = S, I) compounds[87,88] also proceeds via nitrene generation (Scheme 13).



Scheme 13

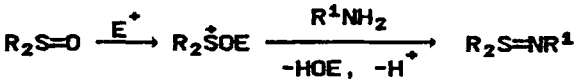
2.1.1.4. *Oxidative Cyclization of Amino Sulfides* Aromatic amines containing an alkylthio group in *o*-position form, when treated with *N*-chlorosuccinimide, cyclic aminosulfonium salts which are converted to cyclic sulfimides[89,90] in the presence of base (Scheme 14).



Scheme 14

2.1.2. Synthesis of Sulfimides from Sulfoxides

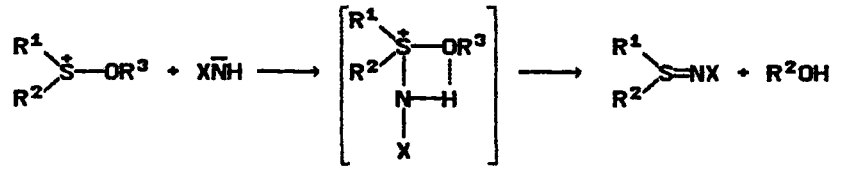
2.1.2.1. Condensation of Sulfoxides with Amides and Amines in the Presence of Activating Electrophilic Reagents This method hinges upon the generation of active sulfonium salts as a result of electrophilic attack on the sulfoxide oxygen which thus is incorporated into a good leaving group (Scheme 15).



Scheme 15

Phosphorus pentoxide,[91] trifluoroacetic anhydride,[91,92] sulfur trioxide, sulfuric acid, and boron trifluoride[93] are used as activating electrophiles. Sulfonic and carboxylic acid amides and certain amines are used as N-nucleophiles. A number of sulfimides have been obtained by the reaction of sulfonic and carboxylic acid sodio amides with alkoxysulfonium salts.[65,94]

The reaction is stereospecific and proceeds with retention of the sulfur atom configuration due, in the opinion of this author, to the formation of an intermediate four-membered cyclic compound stabilized by an intramolecular hydrogen bond (Scheme 16).

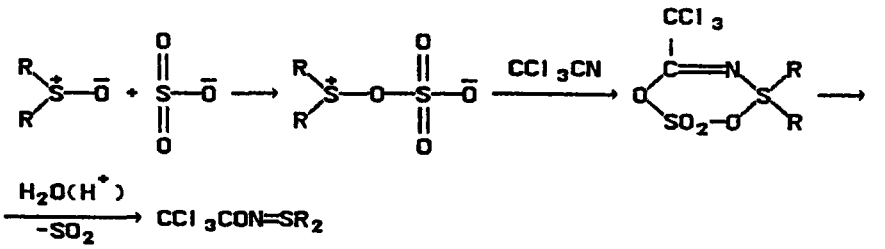


R^1 = 2-$MeOC_6H_4$, R^2 = Ph; R^3 = Me-(p-menthyl)-Pr-*i*,

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

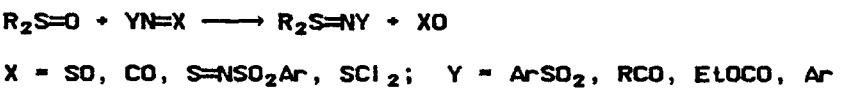
Scheme 16

The sulfonium salts formed in the reaction of sulfoxides with sulfur trioxide react with nitriles to form sulfimides.[95] The likely mechanism of this reaction involves attack by the electron deficient carbon atom of the nitrile group on one of the oxygen atoms in the sulfonium salt and takes place only with nitriles containing strong electron acceptor groups (Scheme 17).



Scheme 17

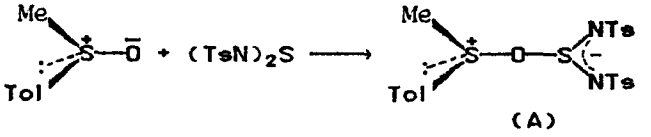
2.1.2.2. *Condensation of Sulfoxides with* N-*Substituted Amides* The condensation of sulfoxides with some *N*-substituted amides containing groups with polar double bonds as substituents proceeds in the absence of activating electrophilic reagents (Scheme 18).[96–99]



X = SO, CO, $S{=}NSO_2Ar$, SCl_2; Y = $ArSO_2$, RCO, EtOCO, Ar

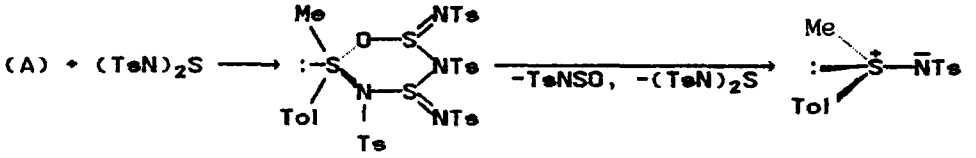
Scheme 18

Its mechanism has been studied in detail in the reaction of methyl-*p*-tolyl sulfoxide with *N*,*N*′-bis-(*p*-toluenesulfonyl)sulfur diimide.[100] The attack by the electron deficient atom of the polar group on the sulfoxide oxygen forms a sulfonium salt the further transformation of which depends on the nature of the solvent (Scheme 19).



Scheme 19

In pyridine, reaction of the sulfonium salt with a second molecule of sulfur diimide results in the formation of a six-membered transition state, the transformation of which to the sulfimide is accompanied by inversion of the configuration of the chiral sulfur atom (Scheme 20).

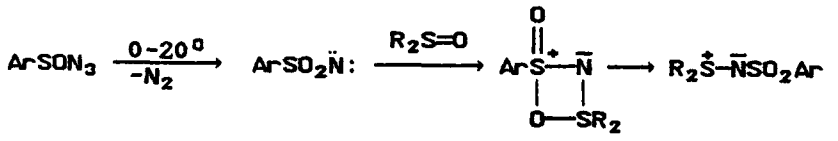


Scheme 20

In benzene the reaction proceeds *via* a four-membered transition state with retention of the configuration of the sulfur atom (Scheme 21).

Scheme 21

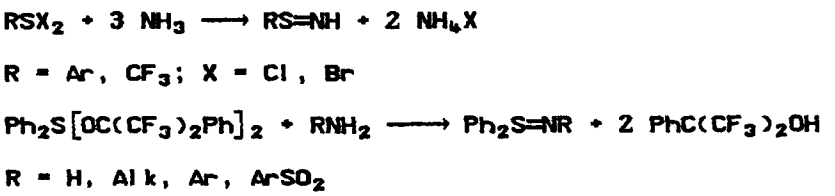
2.1.2.3. *Reaction of Sulfoxides with Arenesulfinyl Azides* Unlike arenesulfonyl azides which form *N*-arenesulfonyl sulfoximides[101] with sulfoxides, arenesulfinyl azides react with sulfoxides to yield *N*-(arenesulfonyl)sulfimides.[102] It is supposed that the intermediately formed arenesulfinyl nitrenes produce with sulfoxides unstable four-membered cyclic compounds en route to the final sulfimides (Scheme 22).



Scheme 22

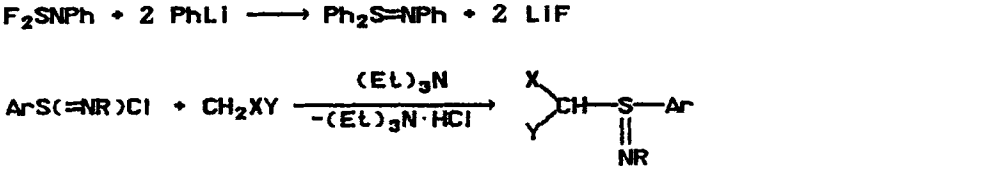
2.1.3. *Use of Other Tetracoordinate Sulfur Compounds in Sulfimide Synthesis*

2.1.3.1. *Nucleophilic Substitution at the Tetracoordinate Sulfur Atom* The nucleophilic substitution of various atoms and groups at a tetracoordinate sulfur atom to obtain sulfimides is used in two versions. The first one involves the nucleophilic substitution of halogen atoms[103,104] or alkoxy groups[103,105,106] to create an S^{IV}=N bond (Scheme 23).



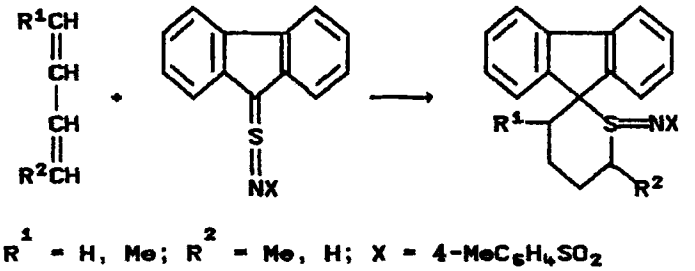
Scheme 23

The second version involves nucleophilic substitution of halogen atoms at the tetracoordinate sulfur atom with formation of an S^{IV}=N bond (Scheme 24).[107,108]



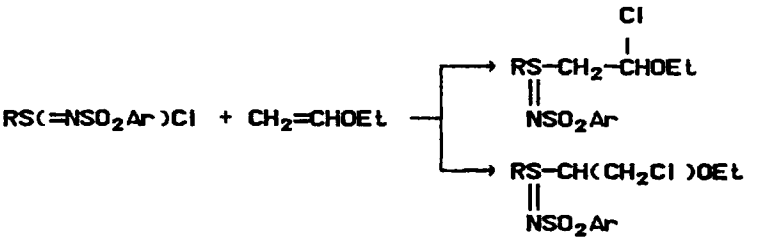
Scheme 24

2.1.3.2. *Reaction of Thione S-Imines with Dienes* It has been shown[109] that *N*-substituted thione *S*-imines containing arenesulfonyl groups are substituents can play the role of active dienophiles in [4 + 2]-cycloadditions with conjugated dienic hydrocarbons to form cyclic sulfimides containing the sulfur atom in the ring (Scheme 25).



Scheme 25

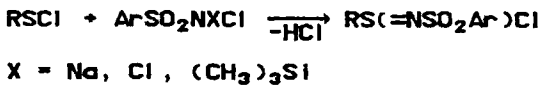
2.1.3.3. *Addition of Iminosulfinic Acids Chlorides to Double Bonds* *N*-(Arenesulfonyl)iminosulfinic acid chlorides relatively easily add to the double bond of ethyl vinyl ether to form mixtures of isomeric sulfimides (Scheme 26).[110]



Scheme 26

2.2. *Synthesis of Iminosulfinic Acid Halides*

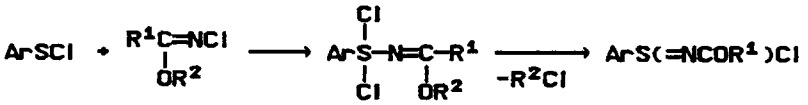
2.2.1. *Oxidative Imination of Sulfenyl Chlorides with* N-*Halo and* *N*,N-*Dihalo Compounds* As shown by Levchenko *et al.*, [21] *N*-arenesulfonyl areneiminosulfinic acid chlorides are formed smoothly by reaction of arenesulfenyl chlorides with *N*-chloro- and *N*,*N*-dichloroarenesulfonamides in anhydrous media (Scheme 27).



Scheme 27

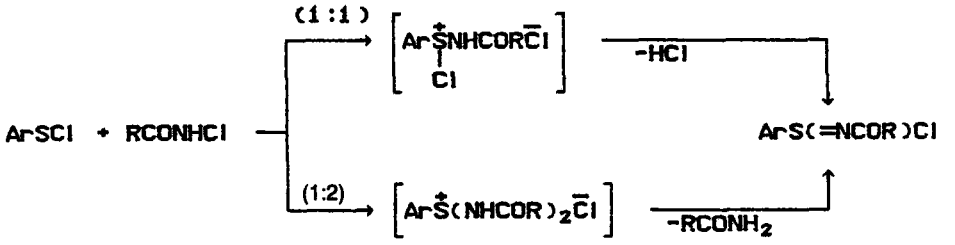
To obtain *N*-substituted iminosulfinic acid chlorides containing other substituents on the nitrogen atom, use is made of *N*,*N*-dichlorourethane and esters of *N*-(chloroimino)carbonic acid,[21] *N*-chloro-*N*-methyl-*t*-butylamine,[111] *N*-chlorocarboxamides,[112] and *N*-chloroketimines.[113]

Arenesulfenyl chlorides have been shown[14] to react with esters of *N*-chloroiminocarbonic acid to yield sulfuranes which form *N*-acyliminosulfinic acid chlorides by loss of alkyl halides (Scheme 28).



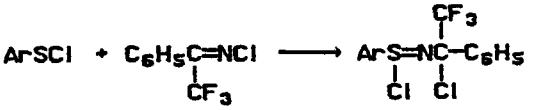
Scheme 28

The intermediates in the reaction of arenesulfenyl chlorides with *N*-chlorocarboxamides,[112] depending on the ratio of reactants, are aryl(acylamino)sulfonium chlorides (Scheme 29).



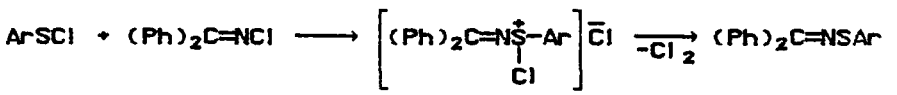
Scheme 29

Arenesulfenyl chlorides react with *N*-chloroketimines in different ways.[113] Formation of the corresponding iminosulfinic acid chlorides was observed when arenesulfenyl chlorides reacted with *N*-chloro(trifluoromethyl)phenylketimine (Scheme 30).



Scheme 30

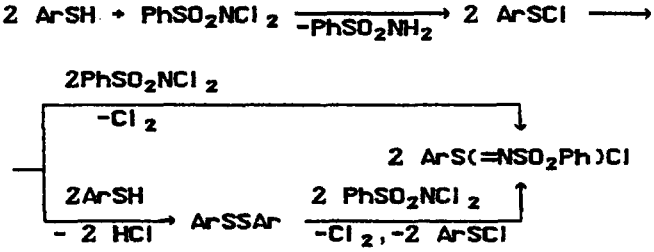
The reaction of arenesulfenyl chlorides with *N*-chlorodiphenylketimine leads to *N*-arenesulfenyldiphenylketimines (Scheme 31).



Scheme 31

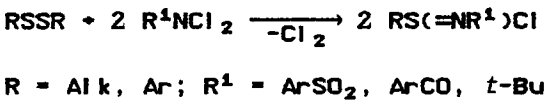
Arenesulfenyl chlorides do not react with *N*-chlorobis(trifluoromethyl) ketimine.

2.2.2. *Oxidative Imination of Thiols and Disulfides with* N,N-*Dihalo Compounds* Depending on the ratio of reagents and the order of mixing the formation of *N*-arenesulfonylareneiminosulfinic acid chlorides in the reaction of thiophenols with *N*,*N*-dichloroarenesulfonamides can proceed in two alternative directions (Scheme 32).[115]



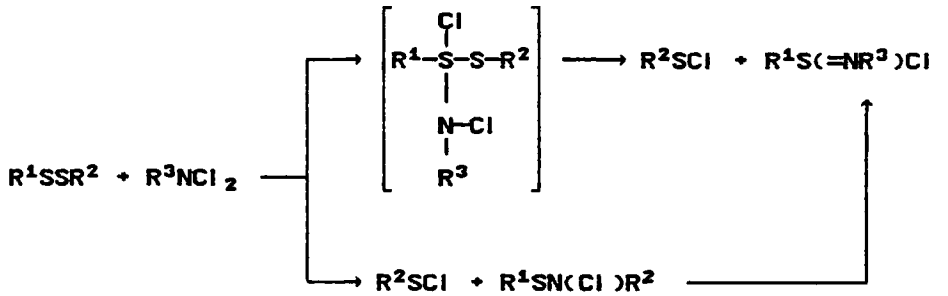
Scheme 32

The intermediate arenesulfonamides decrease the yield of iminosulfinic acid chlorides therefore the synthesis of iminosulfinic acid chlorides from disulfides and *N,N*-dihalo compounds[115-122] is more convenient (Scheme 33).



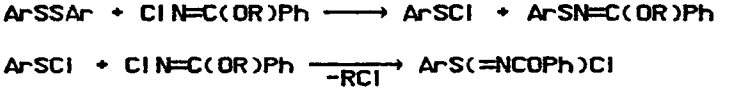
Scheme 33

As shown by Levchenko *et al.*,[120,121] the imination of asymmetric disulfides with *N,N*-dihalo compounds occurs on the more nucleophilic sulfur atom which requires that the incipient sulfenyl chloride attached to the sulfur atom possesses strongly electron withdrawing groups. In the opinion of the authors[121] the formation of iminosulfinic acid chlorides can proceed, in this case, in two alternative directions, yielding tetracoordinate sulfur compounds or *N*-chlorosulfenamides as intermediates (Scheme 34).



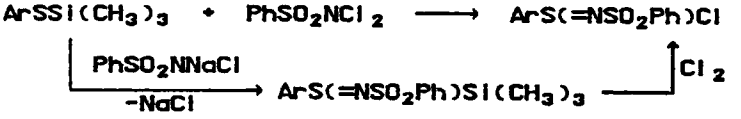
Scheme 34

The latter direction is more likely since the formation of sulfenyl chlorides and the corresponding sulfenamides was also observed in the reaction of disulfides with *N*-chloroimino esters[123] (Scheme 35).



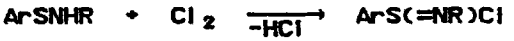
Scheme 35

Trimethylsilyl aryl sulfides[124] react with *N,N*-dihalo compounds in much the same way as asymmetric disulfides (Scheme 36).



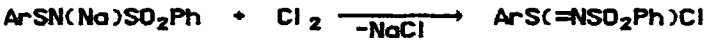
Scheme 36

2.2.3. *Halogenation of Sulfenamides* As illustrated by Markovski *et al.*,[125] *N*-substituted iminosulfinic acid chlorides are formed when *N*-substituted sulfenamides are chlorinated with chlorine in anhydrous organic solvents (Scheme 37).



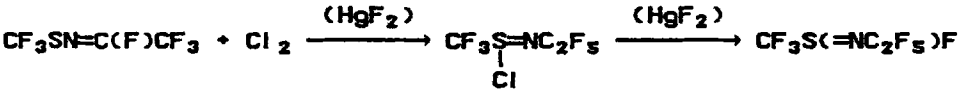
Scheme 37

N-Chloroimides, *N*,*N*-dichloroamides, and *t*-butyl hypochlorite are also used as chlorinating agents. The susceptibility of sulfenamides to chlorination is dependent upon the electron density on the sulfur atom; the presence of electron-acceptor groups at the sulfur or nitrogen atom of sulfenamides impedes this process or makes it impossible. In this connection the use of sulfenamide sodium salts, instead of sulfenamides, considerably increases the ratio of chlorination due to an increase in the electron density on the sulfur atom at the expense of its displacement from the α-N-anionic center (Scheme 38).[126]



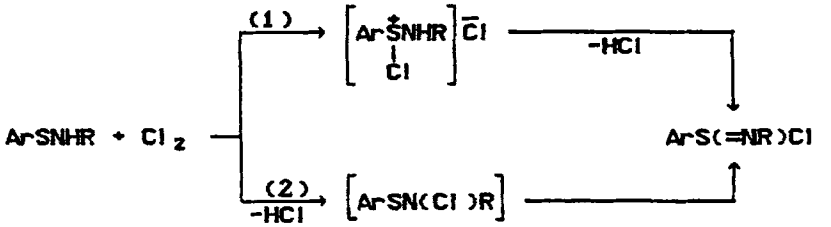
Scheme 38

Sometimes the chlorination of sulfenamides with low electron density on the sulfur atom is performed in the presence of catalysts, *e.g.* mercury(II) difluoride (Scheme 39).[127]



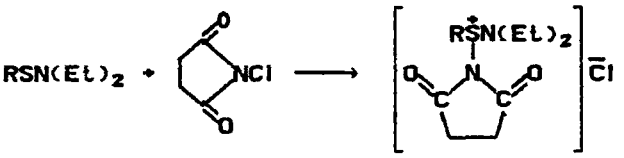
Scheme 39

With regard to the possibility of attack of a chlorine cation on both the sulfur atom and the nitrogen atom, two alternative modes of formation of iminosulfinic acid chlorides in the oxidative chlorination of sulfenamides have been suggested (Scheme 40).[125]

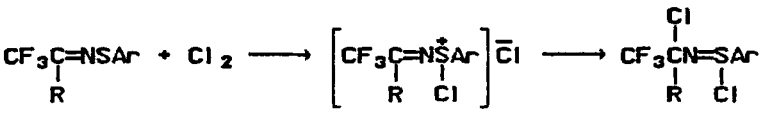


Scheme 40

The first is more likely since *N*-chlorosulfenamides cannot always rearrange to iminosulfinic acid chlorides.[125] At the same time the formation of azasulfonium chlorides was noted in the reactions of *N*,*N*-dialkylsulfenamides with *N*-chlorosuccinimide (Scheme 41)[128] and of *N*-arenesulfenylketimines with chlorine (Scheme 42).[113,129]



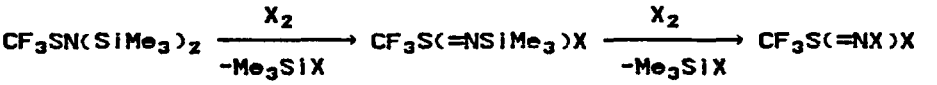
Scheme 41



Scheme 42

Attack of the chlorine cation on the nitrogen atom is likely to occur in the case of low electron density on the sulfur atom, *e.g.* with strong electron-acceptor groups attached to the sulfur atom.

The halogenation of *N*,*N*-bis(trimethylsilyl)trifluoromethanesulfenamide is accompanied by stepwise cleavage of the N—Si bonds and formation of *N*-(trimethylsilyl)trifluoromethaneiminosulfinic acid halides and *N*-(chloro)fluorotrifluoromethaneiminosulfinic acid halides (Scheme 43).[130]



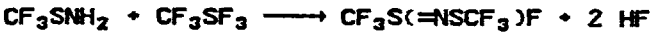
Scheme 43

The chlorination of bis(trifluoromethanesulfenyl)imide involves one sulfur atom only and leads the formation of *N*-(trifluoromethanesulfenyl)trifluoromethaneiminosulfinic acid chloride (Scheme 44).[130]

Scheme 44

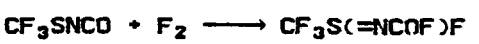
The fluorination of trifluoromethanesulfenamide with trifluoromethylsulfur trifluoride is accompanied by the replacement of one of the amido group hydrogen

atoms with a trifluoromethylthio group and the formation of *N*-(trifluoromethylthio)trifluoromethaneiminosulfinic acid fluoride (Scheme 45).[130]



Scheme 45

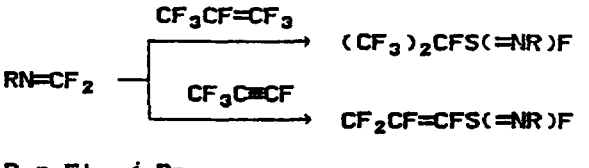
In the literature[131] the preparation of *N*-(fluorocarbonyl)trifluoromethaneiminosulfinic acid fluoride by fluorination of trifluoromethanesulfenyl isocyanate with fluorine has been reported (Scheme 46).



Scheme 46

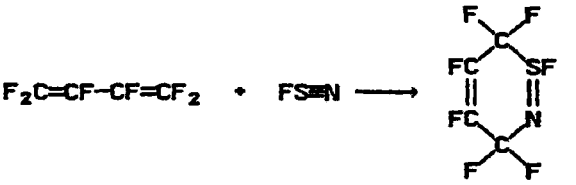
It is evident that in this case the fluorine adds to the N=C bond of trifluoromethanesulfenyl isocyanate and that the *N*-fluoro(fluorocarbonyl)trifluoromethanesulfenamide formed is subsequently isomerized.

2.2.4. *Addition of Tetracoordinate Sulfur Halides to Multiple Bonds* The first representatives of *N*-substituted iminosulfinic acid fluorides were obtained by addition of iminothionyl fluorides to unsaturated perfluorides (Scheme 47).[132]



Scheme 47

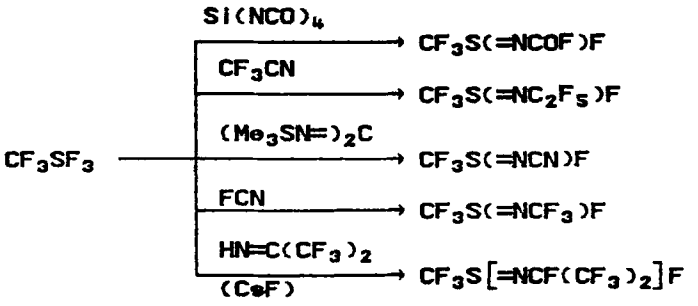
As shown,[133] the addition of thiazyl fluoride to perfluorobutadiene leads to the formation of an iminosulfinic acid fluoride with a cyclic structure (Scheme 48).



Scheme 48

The addition of trifluoromethylsulfur trifluoride to compounds with nitrogen-carbon multiple bonds such as silicon tetraisocyanate,[134] trifluoroacetonitrile,[135] *N*,*N*-bis(trimethylsilyl)carbodiimide,[133] ketimines,[135] and cyanogen fluoride[136] has

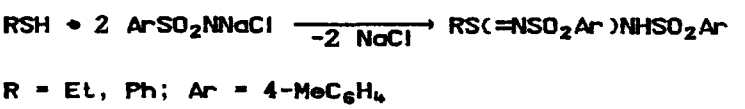
found wide application in the synthesis of *N*-substituted iminosulfinic acid fluorides (Scheme 49).



Scheme 49

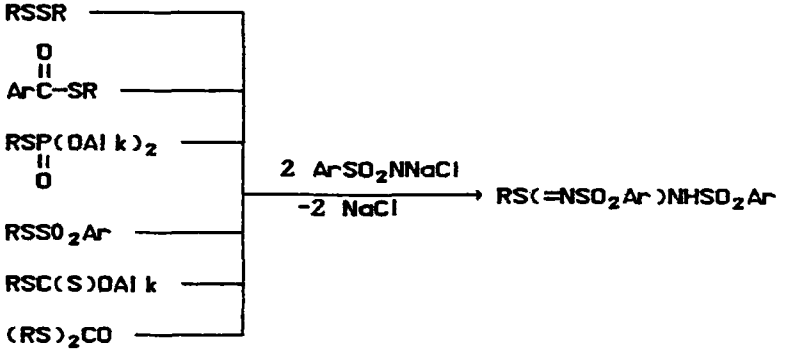
2.3. *Synthesis of Iminosulfinic Acid Amides*

2.3.1. *Oxidative Imination of Thiols and Compounds Containing the Thio Group with* N*-Halo Compounds* The first representatives of iminosulfinic acid amides to become known were *N*-arenesulfonylamides of *N'*-arenesulfonyliminosulfinic acids or *N,N'*-bis(arenesulfonyl)sulfinamidines obtained in 1930 by Klarke *et al.*[137] by the reaction of thiols with *N*-chloroarenesulfonamide salts in aqueous media (Scheme 50).



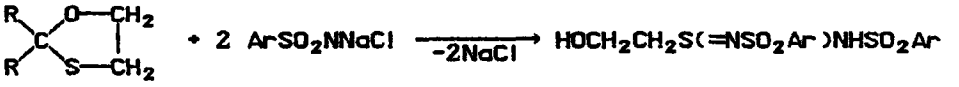
Scheme 50

Later on it could be shown that *N,N'*-bis(arenesulfonyl)sulfinamides are also formed by reaction of *N*-chloroarenesulfonamide salts with disulfides,[138–141] esters of thiocarboxylic acids,[141,142] thiolphosphoric acids,[142] thiolsulfonic acids,[143] xanthogenic acids, and dithiocarbonic acids (Scheme 51).[144]



Scheme 51

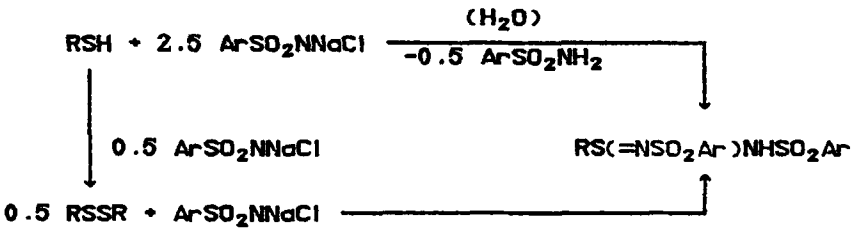
N,N'-Bis(arenesulfonyl)sulfinamidines are also formed by reaction of some unstable sulfur-containing heterocyclic compounds, *e.g.* 1,3-oxathiolanes, with *N*-chloroarenesulfonamide salts in aqueous media (Scheme 52).[145]



Scheme 52

Explaining the low yields of *N,N'*-bis(arenesulfonyl)sulfinamidines in the reaction of thiols with *N*-chloroarenesulfonamide salts the authors[137] suggest that in aqueous media the *N*-chloroarenesulfonamide salts are subject to hydrolysis resulting in the formation of arenesulfonamides though they did not study this reaction in anhydrous media.

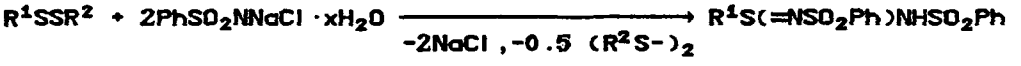
Later on it was shown[144] that the formation of arenesulfonamides in the reaction of thiols with *N*-chloroarenesulfonamide salts has other reasons. The authors[144] established that a portion of the *N*-chloroarenesulfonamide salt is spent to oxidize the thiol prior to the formation of the disulfide, further imination of which brings about the formation of the *N,N'*-bis(arenesulfonyl)sulfinamidine (Scheme 53).



Scheme 53

The formation of disulfides and arenesulfonamides was also observed in the arenesulfonylimination of alkanethiols,[146] arenethiols,[147] 8-mercaptoquinoline,[148] arylcarbamoylmethanethiols,[149] and of alkoxycarbonylmethanethiols.[150] It follows that the iminations of thiols and disulfides with *N*-chloramides are similar and that the first stage of the thiol imination is its oxidation to the disulfide. In this case this stage is not a limiting one since the rate of thiol oxidation to disulfides with various oxidants decreases in the series[151] ArSH > $ROOCH_2SH$ > AlkSH while the reactivity of thiols towards *N*-chloroarenesulfonamide salts changes in the reverse direction and, as shown in the literature,[147] is determined by their acidity. Thiols with pK_a 7 are relatively readily iminated with *N*-chloroarenesulfonamide salts. The reduction of the pK_a of the thiols to 5–6 leads to a decrease of the imination rate and of the yield of *N,N'*-bis(arenesulfonyl)sulfinamidines. Thiols with $pK_a < 5$ are no longer iminated by *N*-chloroarenesulfonamide salts.

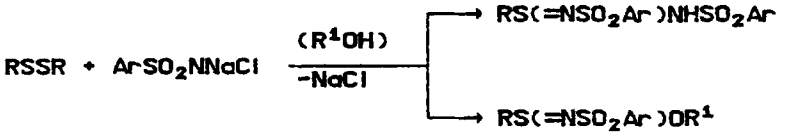
As a rule these thiols have strong electron-acceptor groups on the sulfur atom. As shown,[152] the imination of asymmetric disulfides with *N*-chloroarenesulfonamide salts proceeds at the more nucleophilic sulfur atom. With regard to the acid properties of the corresponding thiols this means that the pK_a value of the thiol corresponding to the RS group being iminated is higher than that of the thiol corresponding to the RS group being removed (Scheme 54).



R^1 = Bu; R^2 = 4-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$

Scheme 54

In the reaction of disulfides with *N*-chloroarenesulfonamide salts in alcoholic media the formation of iminosulfinic acids esters, along with iminosulfinic acid amides, has been noted (Scheme 55).[153,154]



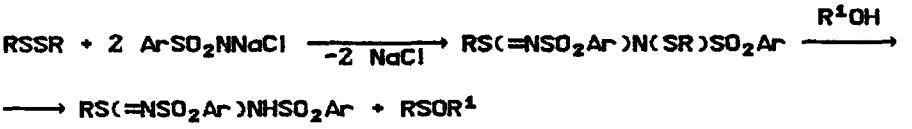
Scheme 55

In the author's opinion[154] these products are due to the reaction of the intermediate iminosulfinic acid chlorides with arenesulfonamide anion and alkoxide anion.

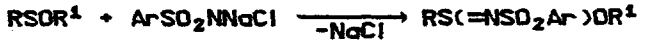
As demonstrated by Levchenko *et al.*[155,156] the reaction of diaryl disulfides with *N*-chloroarenesulfonamide salts in anhydrous media leads to the formation of *N*-arenesulfenyl-*N*,*N*'-bis(arenesulfonyl)sulfinamidines (Scheme 56).

Scheme 56

These compounds are assumed[22,156] to be intermediates in the reaction of disulfides with *N*-chloroarenesulfonamide salts in aqueous media which is quite probable since *N*-arenesulfenyl-*N*,*N*'-bis(arenesulfonyl)-sulfinamidines are readily cleaved in the presence of nucleophilic reagents giving iminosulfinic acid amides in quantitative yields (Scheme 57).[157] In this connection, iminosulfinic acid amides and esters in the reaction of disulfides with *N*-chloroarenesulfonamide salts in an alcohol medium are likely to be formed as a result of the following conversions (Scheme 58).

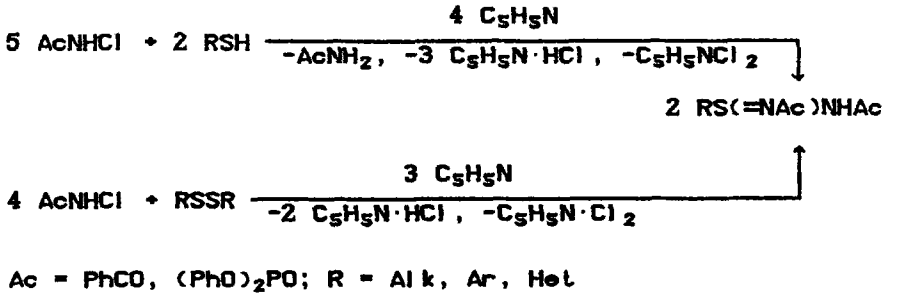


Scheme 57



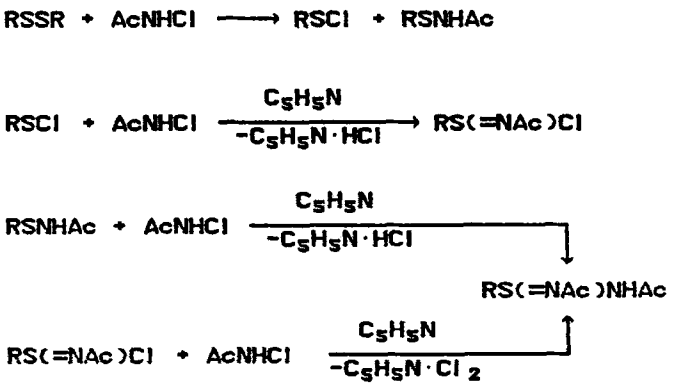
Scheme 58

The imination of thiols and disulfides with *N*-chloramides of carboxylic[158,159] and phosphoric[160] acids is carried out in anhydrous organic solvents in the presence of pyridine (Scheme 59).



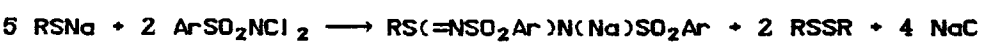
Scheme 59

In this case the formation of iminosulfinic acid amides results from the following transformations (Scheme 60).[122]



Scheme 60

2.3.2. *Oxidative Imination of Sodium Thiolates with* N,N-*Dihalo Compounds* The oxidative imination of sodium thiolates with *N,N*-dihalo compounds with the formation of sodium salts of iminosulfinic acid amides was first studied by Kremlev *et al.*[161] in the case of the reaction of sodium thiophenolate with *N,N*-dichloroarenesulfonamides (Scheme 61).

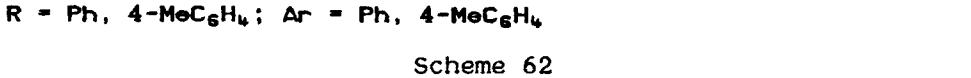


Scheme 61

The reaction has been widely used with alkanethiols,[146] thiourea derivatives,[162] 8-mercaptoquinoline,[163,164] and other heterocyclic compounds.[165] Carboxylic[166,167] and phosphoric[168] acid dichloramides as well as *N,N*-dichlorobis(cyanoethyl)urea[169] are also used as iminating agents.

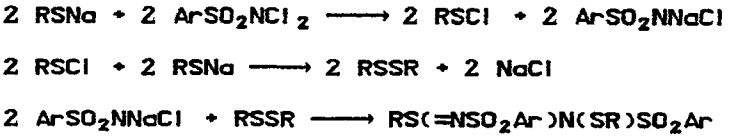
The reactivity of sodium thiolates towards *N,N'*-dihalo compounds has been shown[170] to be influenced by the acidity of the thiols. Sodium salts of thiols with $pK_a > 8$ are readily iminated by *N,N*-dihalo compounds, a decrease in the pK_a value of the thiols to 5–7 reduces the reactivity of sodium thiolates towards *N,N*-dihalo compounds. Sodium salts of thiols with $pK_a < 5$ are no longer iminated by *N,N*-dihalo compounds.

It has been established[157] that *N*-arenesulfenyl-*N,N'*-bis(arenesulfonyl)arenesulfinamidines formed in the reaction of sodium arenethiolates with *N,N*-dichloroarenesulfonamides in a ratio of 4:2 are the intermediates in the above reaction (Scheme 62).



Scheme 62

These compounds are suggested[115] to result from the following conversions (Scheme 63).

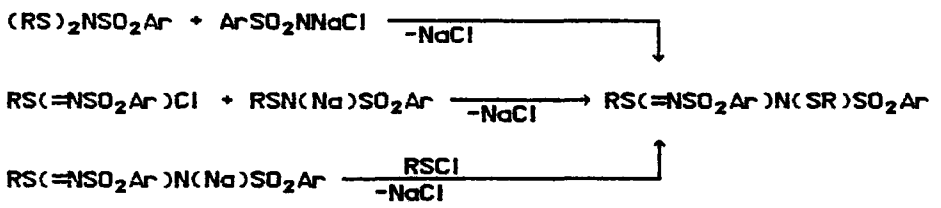


Scheme 63

In the presence of the 5th mole of sodium arenethiolate the *N*-arylsulfenyl-*N,N'*-bis(arenesulfonyl)sulfinamidines are cleaved and yield disulfides and sodium salts of *N,N'*-bis(arenesulfonyl)sulfinamidines (Scheme 64).[157]

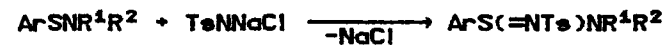
Scheme 64

As shown,[171,172] *N*-arenesulfenyl-*N*,*N'*-bis(arenesulfonyl)sulfinamidines are also generated as a result of the following conversions (Scheme 65).



Scheme 65

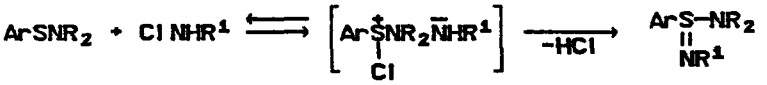
2.3.3. *Oxidative Imination of Sulfenamides with* N-*Halo Compounds* Goerdeler *et al.*[173] demonstrated that sulfenamides $ArSNR^1R^2$ (R^1 = H, Alk; R^2 = Alk) react with chloramine-T according to a general scheme of oxidative imination to form *N*,*N'*-substituted amides of iminosulfinic acids (Scheme 66).



Scheme 66

Sulfenamides of the type ArSNHX [X = $C(=NH)NH_2$, C(=NH)Alk, C(=NH)S-Alk, C(=NH)OAlk] can be iminated with *N*-chloroarenesulfonamide salts,[173] *N*-chlorobenzamide,[174] and *N*-bromobenzamidine.[175] In the presence of bases *N*-acylsulfenamides such as $4\text{-}NO_2C_6H_4SNHAc$ can be iminated with *N*-chloracet- and *N*-chlorobenzamide[176] as well as with *N*-bromobenzamidine;[174] however, the authors attempts[173] to iminate *N*-acyl- and *N*-arenesulfonylarenesulfenamides with *N*-chloroarenesulfonamide salts in acetone proved abortive which can be attributed to the lower electron density of the sulfur atom in these sulfenamides.

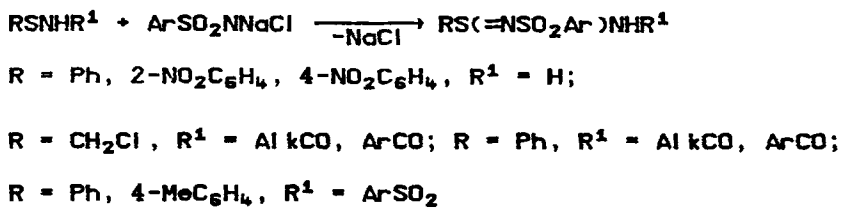
The mechanism of the oxidative imination of sulfenamides with *N*-halo compounds has not been investigated in detail, however, from analogy with the imination of sulfides the chlorine atom of the *N*-halo compound is assumed[177,178] to attack, in an electrophilic manner, the sulfur atom of the sulfenamide to yield the corresponding chlorosulfonium intermediate (Scheme 67).



Scheme 67

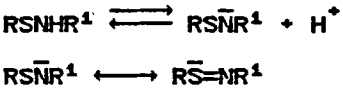
In this connection it is of particular interest that it is possible to activate the sulfur atom towards oxidative imination by creation of an α-N-anionic center[179] which makes it possible to iminate *N*-substituted sulfenamides containing elec-

tron-acceptor groups attached to the sulfur and nitrogen atoms. In this case the choice of the imination condition is determined by the pK_a value of the *N*-substituted sulfenamide.[180] Sulfenamides with $pK_a > 11$ are iminated by *N*-chloroarenesulfonamide salts in acetone in the molecular form (Scheme 68).[181,182]



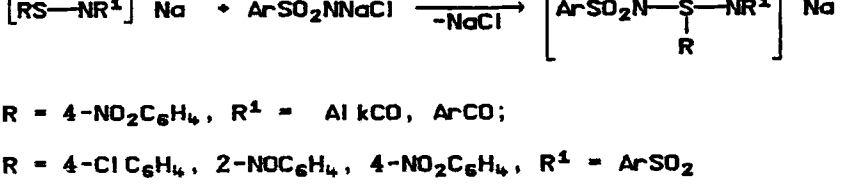
Scheme 68

Sulfenamides with a pK_a value of 8–11 are not iminated in acetone, but in superbasic solvents with a high dielectric constant (aqueous alkaline media, pyridine, etc.) facilitating the dissociation of the sulfenamide to form the α-N-anionic center (Scheme 69).[183,184]



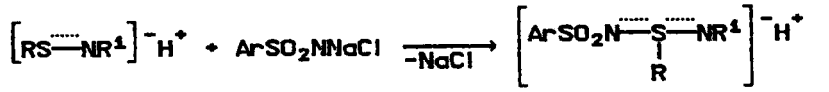
Scheme 69

The sodium salts of such sulfenamides are readily iminated by sulfonic acid sodium chloramides in acetone (Scheme 70).



Scheme 70

Sulfenamides with $pK_a < 8$ are iminated in acetone as well as in aqueous-alkaline media and pyridine since the concentration of sulfenamide N-anion is already rather high, though they are not iminated in benzene, toluene, hexane and solvents of low dielectric constant suppressing the dissociation of sulfenamides (Scheme 71).[150,185,186]

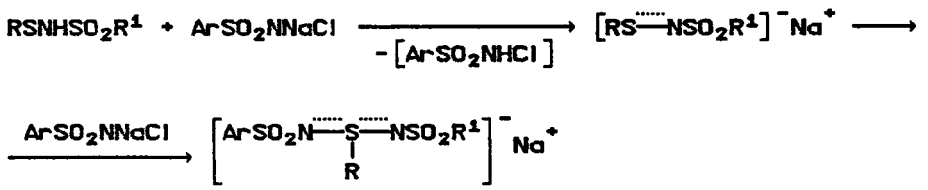


R = EtOCOCCl$_2$, R^1 = ArCO, R = CCl$_3$, R^1 = AlkCO, ArCO;

R = CFCl$_2$, R^1 = AlkCO; R = CF$_2$Cl, R^1 = AlkCO, ArCO

Scheme 71

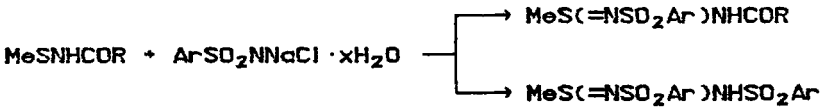
Since in the reaction of sulfenamides with $pK_a < 6$ with *N*-chloroarenesulfonamide salts (*N*-chlorobenzenesulfonamide has pK_a 9.5[187]) initially the sodium salts of sulfenamides are formed; their imination is performed with a reagent ratio of 1:2 (Scheme 72).[180,188]



R = 2,4-(NO$_2$)$_2$C$_6$H$_3$, CCl$_3$

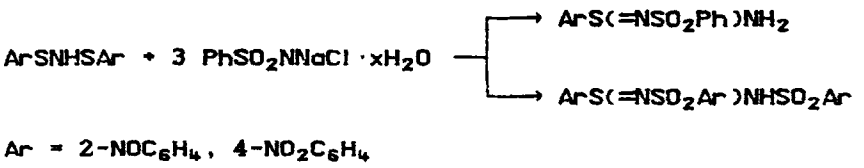
Scheme 72

The direction of the reaction of *N*-acyl-4-nitrobenzenesulfenamides with *N*-chloroarenesulfonamide salts depends on the reaction conditions: these sulfenamides are iminated in aqueous medium whereas in pyridine the reaction is accompanied by S—N bond breaking and the formation of symmetric *N*,*N*′-bis(arenesulfonyl)-4-nitrobenzenesulfinamides.[184] A similar symmetrization has also been observed[189] in the reaction of *N*-acylmethanesulfenamides with *N*-chloroarenesulfonamide salts in acetone (Scheme 73).



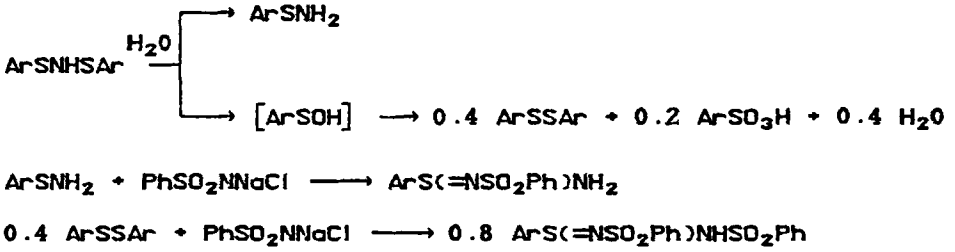
Scheme 73

This process has been studied in more detail in the reaction of *N*-chloroarenesulfonamide salts with bis(arenesulfenyl)imides the products of which are also mixtures of *N*,*N*′-bis(arenesulfonyl)arenesulfinamidines and *N*-arenesulfonylarenesulfinamidines (Scheme 74).[190]



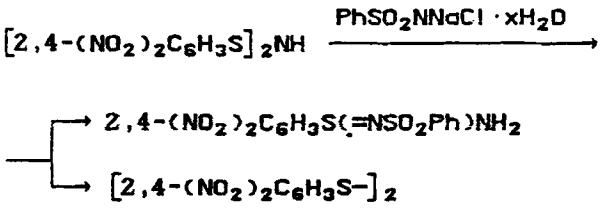
Scheme 74

The formation of the product mixture is explained by two factors: first, the low rate of sulfenamide imination due to the low electron density on the sulfur atoms and the impossibility of its compensation by the formation of an α-*N*-anionic center because bis(arenesulfenyl)imides are relatively weak NH-acids with pK_a 10.8;[190] second, the lability of the sulfur-nitrogen bond, its breaking in the presence of the water of crystallization contained in the *N*-chloroarenesulfonamide salt giving diaryl disulfides and arenesulfenamides further imination of which leads to the reaction products (Scheme 75).



Scheme 75

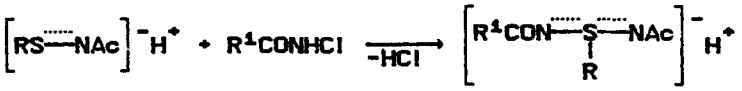
This concept was supported in a study of the reaction of bis(2,4-dinitrobenzenesulfenyl)imide with chloramine-B in acetone yielding *N*-benzenesulfonyl-2,4-dinitrobenzenesulfinamidine and bis-(2,4-dinitrophenyl) disulfide which, as known,[170] is not iminated by chloramine-B (Scheme 76).



Scheme 76

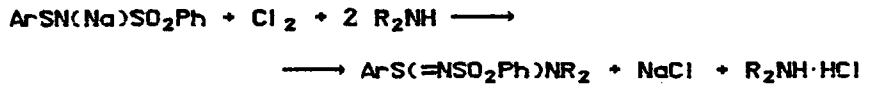
The imination of *N*-acyl- and *N*-arenesulfonylsulfenamides with carboxylic acid *N*-chloroamides[191,192] is carried out in the presence of organic bases which not

only act as acceptors of hydrogen chloride but also favor the dissociation of the starting sulfenamides (Scheme 77).



Scheme 77

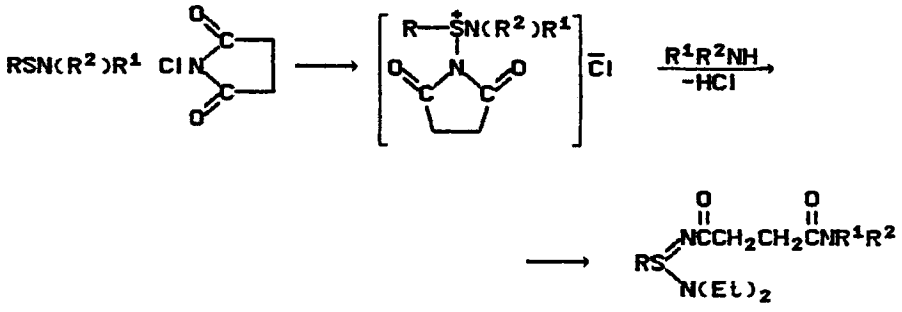
2.3.4. *Oxidative Amidation of Sulfenamides* The chlorination of sodium salts of *N*-arenesulfonylarenesulfenamides with chlorine in the presence of dialkylamines gives *N,N*-dialkyl-*N'*-arenesulfonylarenesulfinamidines (Scheme 78).[193]



Scheme 78

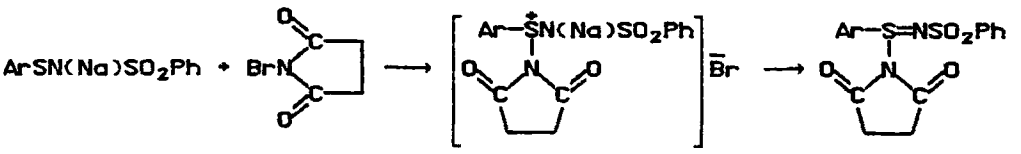
The mechanism of this reaction has not been studied but it is quite possible that chlorosulfonic salts or *N*-arenesulfonyliminosulfinic acid chlorides are intermediates in this reaction.

2.3.5. *Reaction of Sulfenamides with* N-*Halosuccinimides* Two methods for the preparation of iminosulfinic acid amides with sulfenamides and *N*-halosuccinimides as the starting compounds have been reported in the literature.[128,194] One of these[128] involves the reaction of *N,N*-dialkylsulfenamides with *N*-chlorosuccinimide to yield azasulfonium chlorides. Amines then cleave the succinimide ring with formation of iminosulfinic acid amides (Scheme 79).



Scheme 79

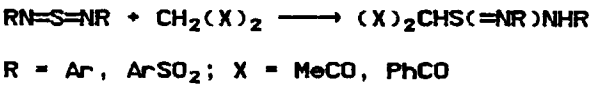
The other method[194] consists of the reaction of the sodium salts of *N*-arenesulfonylarenesulfenamides with *N*-bromosuccinimide yielding azasulfonium bromides which finally lose sodium bromide (Scheme 80).



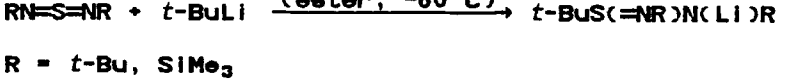
Scheme 80

2.3.6. *Reaction of Sulfur Diimides with CH-Acids* In the case of nucleophilic addition of a CH-acid to one of the S=N bonds of sulfur diimides,[195,196] iminosulfinic acid amides are formed in relatively good yields (Scheme 81).

With weak CH-acids use is made of their lithium salts (Scheme 82).[197]



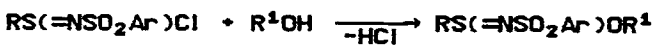
Scheme 81



Scheme 82

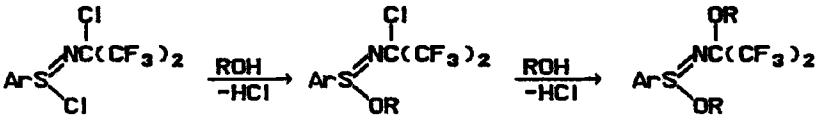
2.4. *Synthesis of Iminosulfinic Acid Esters*

2.4.1. *Reaction of Iminosulfinic Acid Chlorides with Alcohols* *N*-Arenesulfonyliminosulfinic acid esters are rather easily obtained by the reaction of *N*-arenesulfonyliminosulfinic acid chlorides with alcohols or alkoxides (Scheme 83).[198]



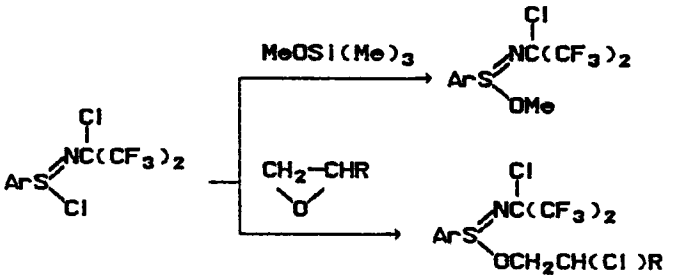
Scheme 83

The replacement of the chlorine atoms by alkoxy groups in *N*-(α-chloroalkyl)areneiminosulfinic acid chlorides proceeds stepwise, first on the sulfur atom and then on the carbon atom (Scheme 84).[113,129]



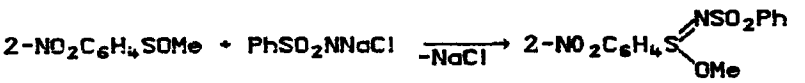
Scheme 84

Sometimes use is made of siloxanes and epoxy compounds instead of alcohols (Scheme 85).



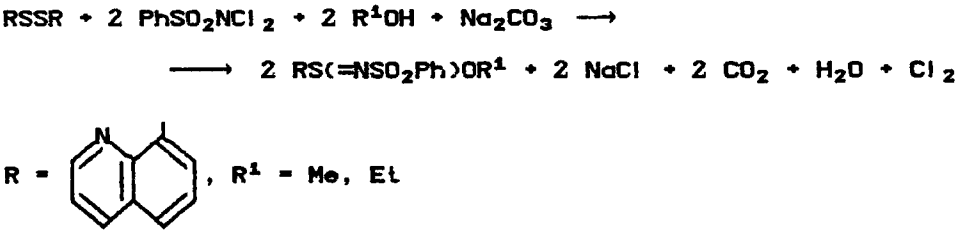
Scheme 85

2.4.2. *Oxidative Imination of Sulfenic Acid Esters with* N-*Halo Compounds* Esters of *N*-benzenesulfonyl-2-nitrobenzeneiminosulfinic acid have been obtained by oxidative imination of 2-nitrobenzenesulfenic acid esters with chloramine B (Scheme 86).[198]



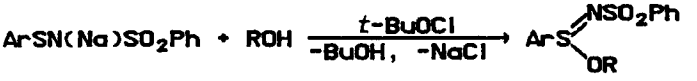
Scheme 86

2.4.3. *Oxidative Imination of Disulfides with* N,N-*Dihalo Compounds* Esters of *N*-benzenesulfonyl-8-quinolineiminosulfinic acid are formed by the reaction of bis-(8-quinolyl) disulfide with *N*,*N*-dichloroarenesulfonamides in alcoholic media in the presence of alkali (Scheme 87).[199]



Scheme 87

2.4.4. *Oxidative Alkoxylation of Sulfenamides* It has been established[200] that esters of *N*-arenesulfonylareneiminosulfinic acids are readily obtained by chlorination of the sodium salts of *N*-arenesulfonylarenesulfenamides with *t*-butyl hypochlorite in alcoholic media (Scheme 88).



Scheme 88

3. PHYSICOCHEMICAL PROPERTIES AND STRUCTURE

3.1. *Physicochemical Properties and Structure of Sulfimides*

3.1.1. *S=N Bond Nature and Sulfimide Structure* There is no unified concept of the nature of the S=N bond in sulfimides and other iminosulfinic compounds despite special emphasis on this problem in papers.[201-221] This is due to the fact that the S=N bond differs from the normal double bond since the overlapping of p-atomic orbitals is energetically disadvantageous for the elements of the 3rd and subsequent periods of the Periodic Table. At the same time, the structural characteristics indicate definitely that this bond is of a multiple nature, but of low π-order and of a length exceeding the corresponding sum of covalent radii. They are also indicative of high polarity and a low-potential barrier of inner rotation which prevents the formation of diastereomeric compounds due to hindered rotation about the S=N bond. Depending on the nature of the substituents at the sulfur and the nitrogen atoms, the lability of the S=N bond changes over a wide range. An analysis of these factors and the analysis of data on the nature of the E=N bond in other elemento-organic compounds give grounds to conclude that the d-orbitals of the sulfur atom participate in the formation of the S=N bond in sulfimides. This statement includes three major views on the nature of the S=N bond in sulfimides established in the last few years.

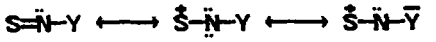
1. The S=N bond is a normal double bond in which the π-bonding is formed by overlapping of p-orbitals of the nitrogen atom and symmetrically corresponding d-orbitals of the sulfur atom.

2. The S=N bond is semipolar with the σ-bond formed by p-atomic orbitals of the sulfur and nitrogen atoms and the other bond is ionic, stabilized by the formation of a complex with charge transfer from the electron-saturated nitrogen atom (=NR group) onto the sulfur atom with a positively charged R_2S group.

3. The S=N bond is a double bond in which the π-bond is stabilized by interaction of p_π- (or n-) orbitals of the nitrogen atom with d_π-orbitals of the sulfur atom or by hyperconjugation brought about by interaction of the unshared electron pair of nitrogen with electrons of antibonding σ-orbitals of the adjacent S—C—bond (n_N-σ_S^*-interaction).

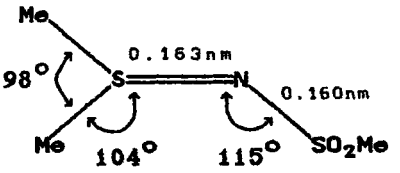
A detailed analysis of the three viewpoints on the nature of the S=N bond involving quantum mechanical calculations, structural and spectral data has failed to bring the authors[221] to an unambiguous conclusion concerning the nature of the S=N bond in sulfimides.

These authors state that sulfimides $R_2S{=}NY$ and isoelectronic analogs are characterized by a mobile π-electronic system including, as an important factor, three d-orbitals the population of which rises with increasing effective electronegativity of the substituents on the sulfur atom and decreases in the presence of π-electron-acceptor groups on the nitrogen atom. The energy of the S=N bond stabilization by d_π-p_π-conjugation is not high, as a rule, and varies depending on the properties of the substituents R and Y. Stabilization is achieved, to a greater degree, by electrostatic interaction of the oppositely charged centers, the R_2S^+ and the $\bar{N}Y$ group. Proceeding from this, the authors[221] suggest that the electronic structure of the S=N bond should be presented in the form of three main resonance structures (Scheme 89).



Scheme 89

The crystal and molecular structures of *S*,*S*-dimethyl-*N*-methanesulfonyl sulfimide and of some *N*-arenesulfonyl sulfimides obtained by X-ray structural analysis have been reported in the literature.[204,205,211,214,221-224] A characteristic feature of these structures is that the tetracoordinate sulfur atom together with the surrounding valence bonds forms a trigonal pyramid which is rather resistant to pyramidal inversion. This is confirmed by the existence of sulfimides with the corresponding substituents in the enantiomeric forms stipulated by the chirality of the sulfur atom. Characteristic bond lengths and angles for a typical representative of sulfimides, *S*,*S*-dimethyl-*N*-methanesulfonyl sulfimide, are presented below (Scheme 90).



Scheme 90

The two C—S^{IV} bonds in this sulfimide in the crystalline state differ in length (0.180 and 0.178 nm) while in solution or in the liquid state these bonds are nearly the same which can be explained by the relatively low rotation barrier of the S=N bond the value of which can be estimated from data calculated for the hypothetical molecule $H_2S{=}NH$ (9.60 kcal·mol^{-1}).[225] The average length of the S^{IV}—C bond is less than the sum of the corresponding covalent radii (0.183 nm)

which can be explained in terms of likely interaction of the methyl groups with the sulfur atom by hyperconjugation. The bond lengths and valence angles of other sulfimides (Table 1) are very close to the ones mentioned above.

A comparison of the physical parameters of the E=N bond (E = S, Se, Te) of sulfimides, selenimides[226] and tellurimides[227] showed an increase in the length of this bond in going from sulfur to tellurium which is in accord with the increase of the covalent radii of the corresponding elements.

According to the literature data[229-231] the polarity of the S^{IV}=N bond varies depending on the nature of groups attached to the nitrogen atom over a wide range leading to dipole moments from 1.56 to 10.1 D. A sharp decrease of the dipole moment when the arenesulfonyl groups at the nitrogen atom is replaced by an aryl group is explained[18] by conjugation of the lone electron pair of the nitrogen atom with π-electrons of the aromatic ring and by involvement of this conjugated system in the delocalization of the negative charge of the nitrogen atom.

3.1.2. *Spectral Properties* The wavenumbers of the S=N bond stretching vibrations in sulfimides (Table 2) occupy a wide spectral range from 750 to 1400 cm^{-1} which allows the conclusion that the polarizability of the π-system of the S=N bond is high. Naturally, the high polarizability of the bond accounts for the great dependence of the absorption band location on the nature of substituents on the sulfur and nitrogen atoms.

The UV absorption spectra of *N*-arenesulfonyl sulfimides[234,242-246] exhibit absorption bands with maxima at 230 nm (log ε 4.0–4.5) and 270 nm (log ε 3.0–4.5). In the UV absorption spectra of *N*-acyl and *N*-ethoxycarbonyl sulfimides[233,234,242,243,247] there is an absorption band with a maximum in the 217–231 nm region (log ε 4.1–4.3). The UV absorption spectra of *N*-aryl-*S*,*S*-dialkyl sulfimides are more complicated due to the presence of absorption maxima at 240–250 nm (log ε 3.6–4.0), 270–280 nm (log ε 3.7–4.0), and 315–325 nm (log ε 3.2–3.6). This character of the UV absorption spectra of *N*-aryl-*S*,*S*-dialkyl

TABLE 1 Lengths and Valence Angles of the S^{IV}=N Bond

Sulfimide	Bond length, nm	Valence angles, deg.		References
		$C\text{-}S^{IV}\text{—}N$	$C\text{-}S^{IV}\text{—}C$	
$Me_2S{=}NC_6H_4NO_2$-2	0.1622	106.5	99.5	214
$(CH_2)_3S{=}NC_6H_4NO_2$-4	0.1649			220
$Me_2S{=}NC_6H_4NO_2$-4	0.1651	104.1		220
$Me_2S{=}NSO_2Me$	0.1627	102.2	98.2	212
$Me_2S{=}NSO_2C_6H_4Me$-4	0.1628	103.8	101	221
$Me_2S{=}NCOPh$	0.1659	104.2	101	204
$Me_2S{=}NCOCCl_3$	0.1667	104.7	99.9	228
$Et_2S{=}NCOCHCl_2$	0.1633	103.8	99.3	221

TABLE 2 Stretching Vibrations of the S=N Bond in Sulfimides

Sulfimide	S=N, cm^{-1}	References
$Ph_2S{=}NH$	910–940	103
$Et_2S{=}NH$	900–910	221
$(p\text{-}MeC_6H_4)_2S{=}NH$	920	221
$Ph_2S{=}NCl$	860	237
$Ph_2S{=}NBr$	860	221
$Ph_2S{=}NMe$	1080, 1140	103
$Ph_2S{=}NBu$	1090	221
$Ph_2S{=}NBu$	1030	221, 232, 233
$Me_2S{=}NCOMe$	797	232
$Me_2S{=}NCOPh$	805, 1330	221
$Et_2S{=}NCOCHCl_2$	810, 825	232
$Ph_2S{=}N(C{=}NH)NH_2$	840	238
$Me_2S{=}NCO_2Et$	782, 821	239–242
$Ph(Me)S{=}NSO_2Me$	952	221
$Me_2S{=}NSO_2Me$	954	234–236
$Ph_2S{=}NSO_2Ph$	767, 968, 970	221
$Me_2S{=}NSO_2C_6H_4Me\text{-}p$	750, 956	221
$Ph_2S{=}NSO_2C_6H_4Me\text{-}p$	981	221
$(p\text{-}MeC_6H_4)_2S{=}NSO_2C_6H_4Me\text{-}p$	970	221

TABLE 3 Chemical Shift of the Methyl Group Protons of *S,S*-Dimethyl sulfimides

Sulfimide	Chemical shift (δ)	References
$Me_2S{=}NH$	2.05	248
$Me_2S{=}NSO_2C_6H_4Me\text{-}4$	2.68	249
$Me_2S{=}NSO_2CF_3$	3.03	250
$Me_2S{=}NCOPh$	2.76	251
$Me_2S{=}NCO_2Et$	2.71	239
$Me_2S{=}NCOCHCl_2$	2.80	252

sulfimides is caused by conjugation of the S=N bond electrons with the π-electrons of the aromatic ring.

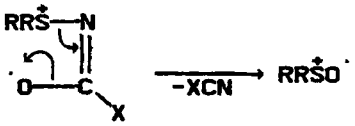
The position of the signals of the methyl group protons in the NMR spectra of *S,S*-dimethyl sulfimides depends on the nature of the groups on the nitrogen atom (Table 3).

The mass spectrum of *S,S*-diphenyl sulfimide[247,252] shows peaks of ionized molecules of diphenyl sulfide (*m/z* 186) and thiophenol (*m/z* 109). The formation of a peak in the spectra of *N*-alkyl-*S,S*-diphenyl sulfimides at *m/z* 200 has also been reported.[253] The mass spectra of *N*-alkyl-*S,S*-diphenyl sulfimides[253] and *N*-aryl-*S,S*-dimethyl sulfimides[67,103] lack molecular ion peaks. The base peaks correspond to the ionized molecules of the sulfides and of the *N*-unsubstituted sulfimides. The primary fragmentation of the molecular ions of *N*-acyl sulfimides[234,243,247] and other carbonyl-containing sulfimides is the elimination of the group bound to the carbonyl group (Scheme 91).

X = Me, Ph, OEt, NHPh

Scheme 91

The appearance of a sulfoxide ion peak in the mass spectra of *N*-acetyl and *N*-benzoyl sulfimides is explained[234,254] by rearrangement of the primary ion (Scheme 92).



Scheme 92

The mass spectral fragmentation of *N*-arenesulfonyl sulfimides involves the formation of SO_2, R_2SNSO and other fragments.

3.2. *Physical and Spectral Properties of Iminosulfinic Acid Derivatives*

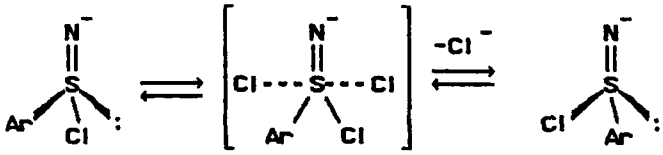
3.2.1. *Physical and Spectral Properties of Iminosulfinic Acid Chlorides* The chlorides of *N*-substituted iminosulfinic acids are colorless or slightly yellowish crystalline substances (the fluorides are liquids in most cases) the stability of which is governed by the nature of the substituents on the sulfur and the nitrogen atom. The *N*-arenesulfonylalkaneiminosulfinic acid chlorides are unstable and used *in situ* without isolation from the reaction mixture. The chlorides of *N*-substituted areneiminosulfinic acids containing arenesulfonyl, acyl, perfluoromethyl and *t*-butyl groups are substituents are relatively stable compounds while the chlorides of *N*-methyl- and *N*-ethylareneiminosulfinic acids could not be isolated[22] because of their instability.

Spectroscopic studies of *N*-substituted areneiminosulfinic acid chlorides have shown[22] that the electron system of the S=N bond is relatively labile and the nature of the substituents on the sulfur and the nitrogen atom affects both the charge value on these atoms and the degree of their double bonding.

The IR absorption bands of the S=N bond stretching vibrations of *N*-substituted iminosulfinic acid chlorides[221] occur in the 950–1200 cm^{-1} region depending on the nature of the substituents. The bathochromic shift of the S=N bond absorption band (950 cm^{-1}) in the case of *N*-acyliminosulfinic acid chlorides is explained[22] by conjugation in the S=N—C=O fragment.

The diastereotopy of the X group in iminosulfinic acid halides $R^1S(=NCH_2R^2)Y$ (X = F, CF_3; R^1 = CF_3, Ar; R^2 = Cl; Y = F, Cl) has been established[256] by ^{19}F NMR spectroscopy. In this case it was noted that in the presence of tetraethylammonium chloride the clearly defined signals of the diastereotopic trifluo-

romethyl groups appear as a broadened signal which, in the authors' opinion,[256] is caused by rapid inversion of the chiral sulfur atom as a result of chloride ion attack (Scheme 93).



Scheme 93

3.2.2. *Physical and Spectral Properties of Iminosulfinic Acid Amides* Iminosulfinic acid amides are colorless or slightly yellowish crystalline substances readily soluble in many organic solvents.

In accordance with the literature data[22,221] the wavenumbers of the S=N bond stretching vibrations in the IR spectra of iminosulfinic acid amides (Table 4) occupy a relatively narrow spectral region from 950 to 1000 cm^{-1}.

A distinctive characteristics of the IR spectra of *N,N'*-disubstituted amides of iminosulfinic acids consists in the fact that the NH-bond stretching vibrations are

TABLE 4 Infrared Spectra of Iminosulfinic Acid Amides[147,180]

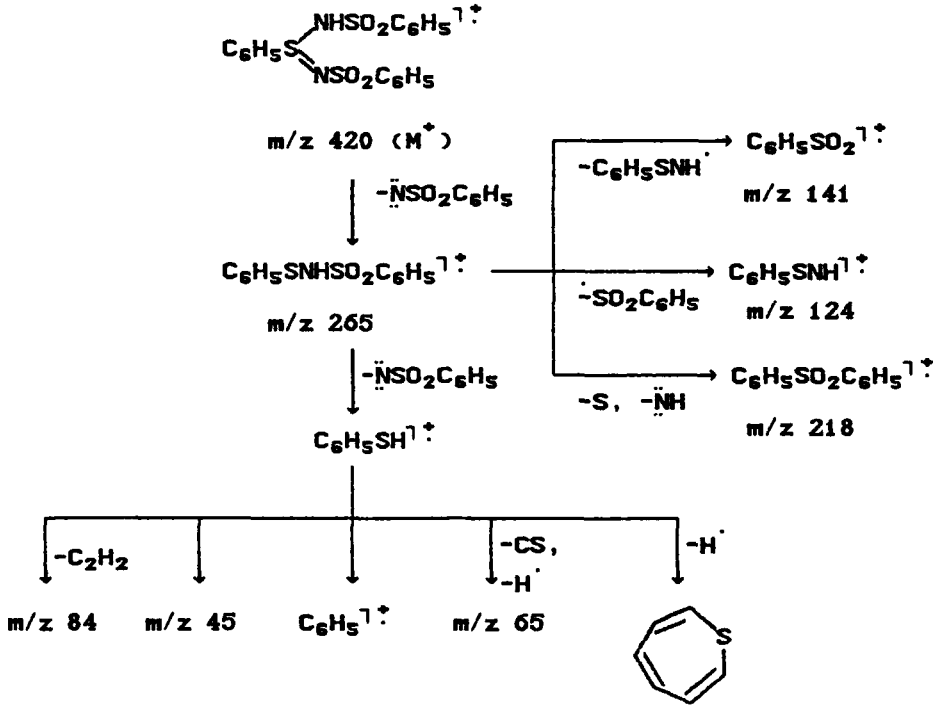
Amide	Stretching vibrations of groups, cm^{-1}					
	NH	C=O	SO_2(as)	SO_2(sym)	NO_2(as)	NO_2(sym)
BuS(=NSO_2Ph)$NHSO_2Ph$	3100–3200			1175		
$C_6H_5CH_2SNHSO_2Ph$ ‖ NSO_2Ph	3050, 3100			1160		
$PhSNHSO_2C_6H_4Me$-4 ‖ NSO_2Ph	3000, 3160		1310	1150	1500	1340
4-$NO_2C_6H_4SNHSO_2Ph$ ‖ NSO_2Ph	3065, 3111		1320	1150	1520	1350
2,4-$(NO_2)_2C_6H_3SNHSO_2Ph$ ‖ NSO_2Ph	3260, 3350		1320	1160	1540	1340
PhS(=NSO_2Ph)NHCOPh	3000, 3060	1680	1320	1160		
$PhSNHCOC_6H_4Me$-4 ‖ NSO_2Ph	3050, 3110	1670	1310	1160		
4-$NO_2C_6H_4SNHCOPh$ ‖ $NSO_2C_6H_4Me$-4	3050, 3100	1670	1310	1150	1530	1350
4-$NO_2C_6H_4SNHCOMe$ ‖ NSO_2Ph	3100, 3180	1680	1310	1150	1520	1320
CCl_3S-(=NSO_2Ph)NHCOPh	3020, 3180	1680	1320	1170		

nearly always represented by two absorption bands: a narrow band in the region of 3000–3200 cm^{-1} and a broad band of low intensity at 3100–3400 cm^{-1}.

The UV spectra of *N,N'*-bis(benzenesulfonyl)arenesulfinamidines 4-RC_6H_4S-(=NSO_2Ph)$NHSO_2Ph$ (R = CH_3, H, Cl, NO_2) show intense absorption bands with maxima at 250–300 nm (log ε 3.8–4.5) the position and intensity of which depend on the nature of substituents R.[170] In case of electron-acceptor substituents a bathochromic shift of the absorption maximum is observed, with electron-donor substituents a hypsochromic shift.

The NH group in the ^1H NMR spectra of iminosulfinic acid amides is gives rise to a signal at δ 8–8.5 (cf. Table 5).[159]

The mass spectra of *N,N'*-disubstituted iminosulfinic acid amides lack molecular ion peaks. The base peaks correspond to arenesulfonyl ions. The primary fragmentation of ionized *N,N'*-bis(benzenesulfonyl)benzenesulfinamidine[170] is elimination of benzenesulfonylnitrene with formation of an intense peak of the *N*-benzenesulfonylbenzenesulfenamide ion (*m/z* 265). Its subsequent breakdown can follow several directions (Scheme 94).



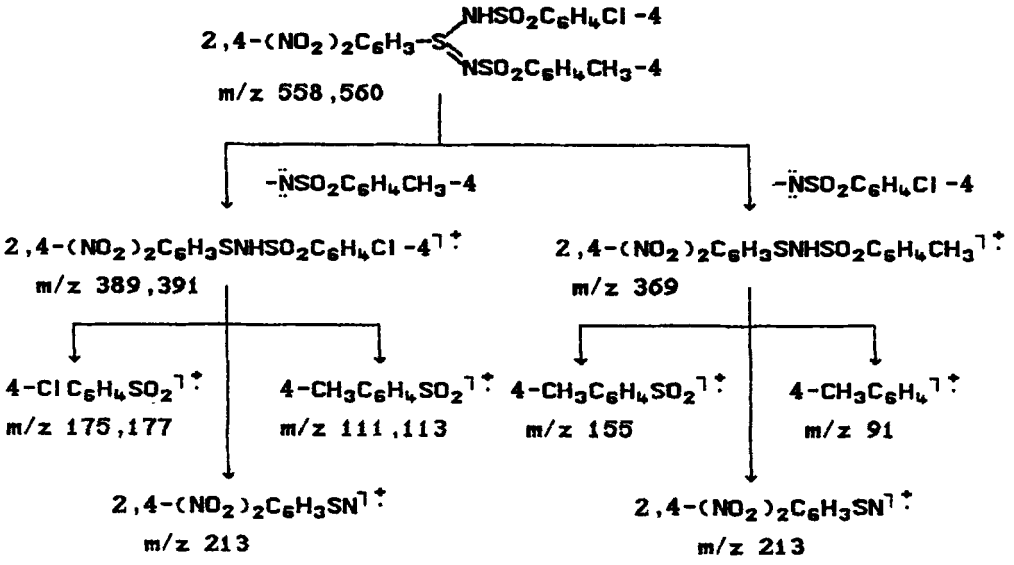
Scheme 94

The identity of the thiophenol ion peak (*m/z* 110) in the mass spectrum is confirmed by its characteristic fragmentation (ions with *m/z* 45, 65, 77, 84, 100). The maximum peaks in the mass spectrum of *N*-(4-chlorobenenesulfonyl)-*N'*-(4-

TABLE 5 ^{1}H NMR Spectra of Iminosulfinic Acid Amides

Amide	Chemical shift of protons (δ)				References
	CH_3	$—CH_2CH_2—$	$—CH_2S$	H_{ar}	
$BuS(=NCOPh)NHCOPh$	0.89 t	1.161 m	3.54 t	7.2–7.9 m	159
$BuS(=NSO_2Ph)NHSO_2Ph$	0.31 t	1.04 m	3.34 t	7.1–7.7 m	147
$PhCH_2S(=NSO_2Ph)NHSO_2Ph$			5.0 s	7.0–7.8 m	147
$2\text{-}NO_2C_6H_4S(=NSO_2Ph)NEt_2$	1.35 t	3.3 g ($—CH_2$)		7.5–7.9 m	193

(methylbenzensulfonyl)-2,4-dinitrobenzenesulfinamidine[180] are the peaks of the aryl moieties $4\text{-}MeC_6H_4^{7+}$ (*m/z* 91) and $4\text{-}ClC_6H_4^{7+}$ (*m/z* 111) as well as the peaks of the arenesulfonyl moieties $4\text{-}MeC_6H_4SO_2^{7+}$ (*m/z* 155) and $4\text{-}ClC_6H_4SO_2^{7+}$ (*m/z* 175). Most likely is also the formation of unstable ions of *N*-arenesulfonyldinitrobenzenesulfenamides (*m/z* 389 and 391) which is in agreement with the fragmentation shown below (Scheme 95).[180]



Scheme 95

3.2.3. *Physical and Spectral Properties of Iminosulfinic Acid Esters* Esters of *N*-arenesulfonyliminosulfinic acids are colorless or slightly yellowish crystalline substances readily soluble in organic solvents, stable to storage. The spectral characteristics of these compounds are not completely understood. In the literature[200] the IR spectra of the methyl and the ethyl ester of *N*-benzenesulfonyl-2-nitrobenzeneiminosulfinic acid comprising the following absorption bands (cm^{-1}): 1525, 1345 (NO_2), 1310, 1140 (SO_2), 980 (S=N) have been described. In the NMR spectrum of *N*-benzenesulfonyl-2-nitrobenzeneiminosulfinic acid methyl

ester there are signals of the protons of the methyl (δ3.61) and aryl groups (δ7.2–8.5).

4. REACTIONS

4.1. *Reactions of Sulfimides*

According to the nature of the change at the S=N bond all reactions involving sulfimides can be divided into three groups: a) reactions not affecting the S=N bond; b) reactions involving conversion of the S=N bond to S^{II}—N and S^{IV}—N bonds; c) reactions proceeding with cleavage of the S=N bond.

4.1.1. *Reactions Not Affecting the S=N Bond*

4.1.1.1. *Basicity of Sulfimides* Owing to the presence of a nitrogen atom with a high electron density sulfimides exhibit basic properties which change over a wide range depending on the nature of the substituents on the nitrogen and the sulfur atom (Table 6).[18] As seen from Table 6, the basicity of *N*-unsubstituted sulfimides is comparable with that of primary amines. These sulfimides, when reacting with the corresponding acids, easily form stable perchlorates,[257,258] hydrochlorides,[70] toluenesulfonates,[241,259] and picrates.[70,260]

N-Acyl sulfimides[261,262] form hydrochlorides when treated with anhydrous hydrogen chloride in organic solvents; *N*-alkyl and *N*-ethoxycarbonyl-*S*,*S*-

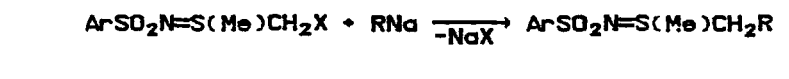
TABLE 6 pK_a Values of Sulfimide Conjugated Acids[18]

Sulfimide	pK_a
4-MeC_6H_4S(=NH)Ph	8.79
2-Me-C_6H_4S(=NH)Ph	8.70
Ph_2S=NH	8.56
4-ClC_6H_4S(=NH)Ph	8.05
2-$NO_2C_6H_4S$(=NH)Ph	7.96
4-$NO_2C_6H_4S$(=NH)Ph	7.30
Me_2S=NH	4.28
Et_2S=NTs	4.70
Me_2S=NTs	0.57
4-$MeOC_6H_4S$(=NTs)Me	−1.78
PhS(=$NSO_2C_6H_4$OMe-4)Me	−2.13
PhS(=NTs)Me	−2.23
4-$MeOC_6H_4S$(=NTs)Me	−2.26
PhS(=NSO_2Ph)Me	−2.36
4-ClC_6H_4S(=NTs)Me	−2.32
PhS(=$NSO_2C_6H_4$Cl-4)Me	−2.55
3-ClC_6H_4S(=NTs)Me	−2.48
3-$NO_2C_6H_4S$(=NTs)Me	−2.85
4-$NO_2C_6H_4S$(=NTs)Me	−2.93
PhS(=$NSO_2C_6H_4NO_2$-4)Me	−3.00
Ph_2S=NTs	−3.60

diphenyl sulfimides[56,103] decompose under these conditions. Hydrophilic picrates are also formed by *N*-substituted sulfimides containing aryl,[67,263] hetaryl,[264] imidoyl,[265,266] phthalimido,[267] and sulfonyl[268] groups. The expected dependence between the pK_a and the Hammett σ-constants of the arenesulfonyl group substituents ($\rho = +0.82$) has been found for a series of *N*-arenesulfonyl-*S*-phenyl-*S*-methyl sulfimides;[269] and one between the pK_a and the Hammett σ-constants of the aryl group substiuents ($\rho = +0.89$) for a series of *N*-tosyl-*S*-aryl-*S*-methyl sulfimides.[30]

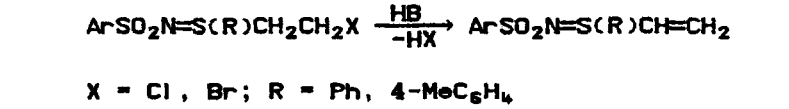
In a reaction with Pd(II) and Pt(II) salts *N*-aryl-*S*,*S*-dimethyl sulfimides produce complexes.[251,270,271] *N*-Benzoyl-*S*,*S*-dimethyl sulfimide forms an orange crystalline complex $[(PPh_3)_2PdCl_2 \cdot Me_2SNCOPh]$ in its reaction with [bis(triphenylphosphine)palladium] dichloride.

4.1.1.2. *Modification of Substituents on the Sulfur and the Nitrogen Atom* The directed chemical modification of various groups on the sulfur and the nitrogen atom in sulfimides is widely used in the synthesis of new types of these compounds. Particularly convenient as starting materials are *S*-(haloalkyl sulfimides which can be readily converted to new types of sulfimides by nucleophilic replacement of the halogen atoms[272] or by dehydrohalogenation (Scheme 96).[273]



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

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

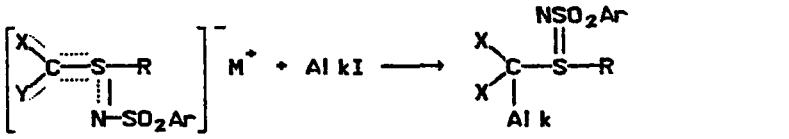


$ArSO_2N{=}S(R)CH_2CH_2X \xrightarrow[-HX]{HB} ArSO_2N{=}S(R)CH{=}CH_2$

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

Scheme 96

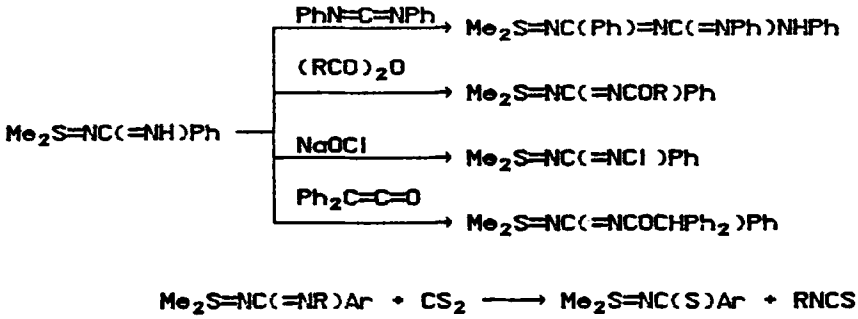
The replacement of the cation in the metal salts of *N*-arenesulfonyl sulfimides with alkyl groups also leads to new types of sulfimides (Scheme 97).[48,51-53]



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

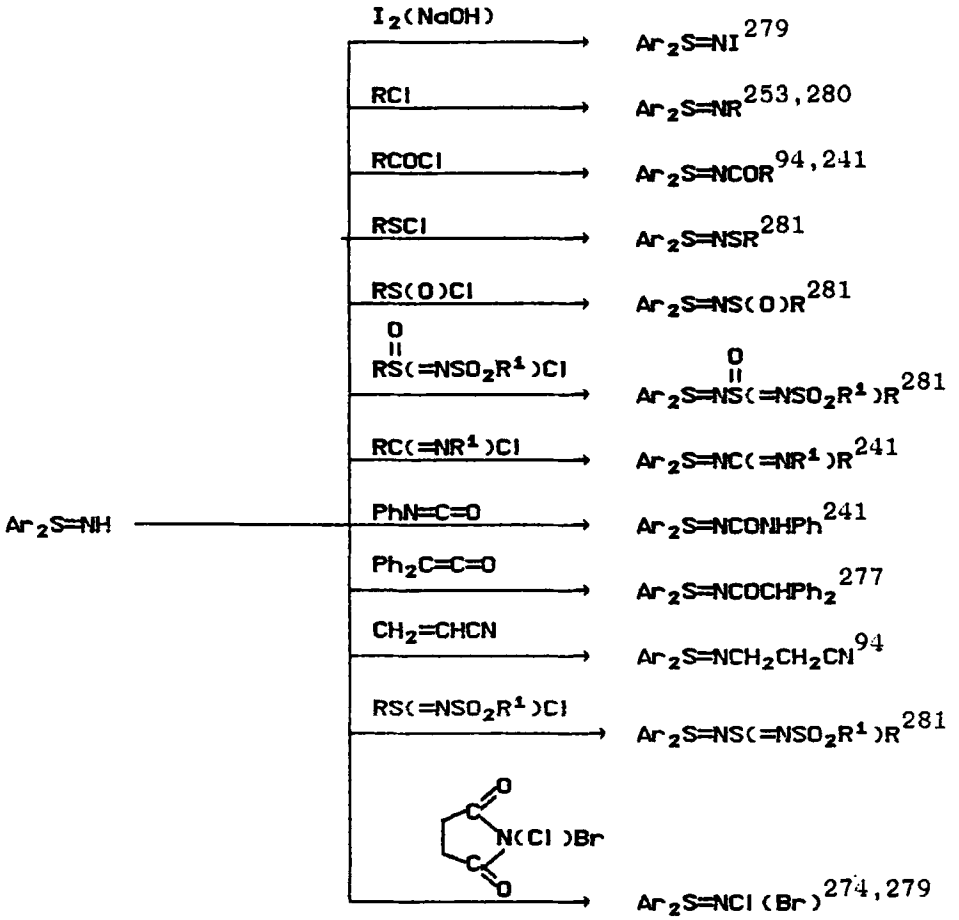
Scheme 97

Some examples of modification of groups attached to the nitrogen atom of *N*-substituted sulfimides are provided by reactions of these groups with different reagents described in[57,274,275] (Scheme 98).



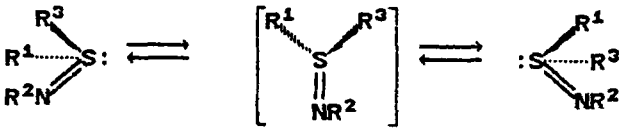
Scheme 98

For the synthesis of new types of *N*-substituted sulfimides use is often made of *N*-unsubstituted sulfimides formed by acid cleavage of the S^{VI}-N bond in *N*-arenesulfonyl sulfimides when they react with 90% sulfuric acid (Scheme 99).[241,276,279]



Scheme 99

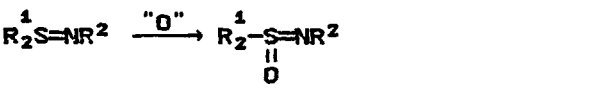
4.1.1.3. *Thermal Racemization of Sulfimides* Sulfimides with different substituents on the sulfur atom can exist in enantiomeric forms due to the sulfur atom chirality. Enantiomer interconversion occurs with rising temperature by a pyramidal inversion mechanism via a planar transition state (Scheme 100).[282]



Scheme 100

Kinetic investigations of the thermal racemization of optically active sulfimides 2-$MeOC_6H_4S(=NR)Ph$ (R = $PhSO_2$, 4-$MeC_6H_4SO_2$, 4-$MeOC_6H_4SO_2$, MeCO, PhCO, CF_3CO, etc.) at 75 °C in chloroform have shown that, along with the known factors affecting the thermal racemization rate (solvent type, steric factors, etc.), an important role is played by the nature of the groups on the nitrogen atom. Strong electron-acceptor groups on the nitrogen atom reduce the thermal racemization rate. For example, the rate of thermal racemization of *N*-tosyl sulfimides is a factor of 15 lower than that of *N*-trifluoroethanoyl sulfimides. In the authors' opinion,[283] this happens because strong electron-acceptor groups hinder 2p-3d transitions when the S=N bond is being formed in the transition state and the repulsion of the lone electron pairs essentially reduces the electron density on the pyramidal nitrogen atom of sulfimides. Therefore, *N*-substituted sulfimides containing weak electron-acceptor groups as substituents adopt a configuration near to planar. The pyramidal inversion rate decreases with a decrease in the wavenumbers of the S=N bond absorption stretching vibrations in the IR spectra which indicates that the increase in the dipolar nature of the S=N bond increases the pyramidal inversion barrier.

4.1.1.4. *Oxidation of Sulfimides* As a rule, sulfimides are resistant to the action of oxidants and are oxidized only by strong oxidants to yield sulfoximides (Scheme 101).

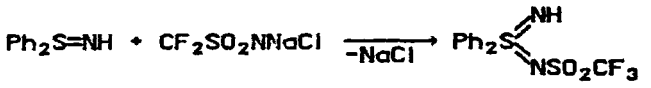


R^1 = Alk, Ar; R^2 = H, $ArSO_2$, RCO, ROCO

Scheme 101

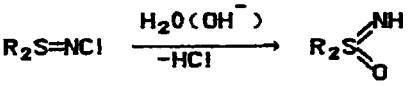
Potassium permanganate,[94] peracids,[241,281] ruthenium tetraoxide,[284] hydrogen peroxide in alkaline medium,[285] and sodium hypochlorite[286,287] are used most fre-

quently as oxidants. For oxidations in two-phase media use is made of phase transfer catalysts such as $Bu_4N{\cdot}X$ (X = Cl, Br, ClO_4, HSO_4), $PhCH_2N(Et)_3Cl$, $C_{12}H_{15}N(Me)_3Cl$, etc.[286,287] It has been shown[288] that *N*-unsubstituted sulfimides are subject to oxidative imination under the action of the sodium salts of *N*-chlorosulfonamides (Scheme 102).



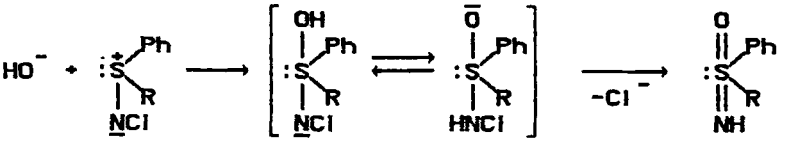
Scheme 102

4.1.1.5. *Alkaline Hydrolysis of Sulfimides* The hydrolytic cleavage of sulfimides in the presence of mineral acids has long been known and well studied. As a rule, this results in the formation of the corresponding sulfoxides and the starting *N*-nucleophiles irrespective of the structure of the sulfimide. The hydrolysis of sulfimides in the presence of bases has not been studied properly. The composition and structure of the products of such hydrolyses depend frequently on various factors, primarily the structure of the sulfimide. The alkaline hydrolysis of *N*-(*p*-toluenesulfonyl)tetrahydrothiophene sulfimide in alcoholic media,[289] for example, results in the formation of the corresponding 2-alkoxytetrahydrothiophene and *p*-toluenesulfonamide. The alkaline hydrolysis of *N*-chloro sulfimides in aqueous medium leads to *N*-unsubstituted sulfoximides (Scheme 103).[278]



Scheme 103

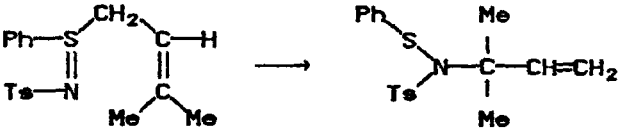
The reaction is stereospecific and with optically active *N*-chloro sulfimides proceeds with 99% retention of the sulfur atom configuration. The hydrolytic mechanism includes a nucleophilic attack on the sulfur atom by the hydroxide anion resulting in a transition state stabilized by abstraction of a chloride ion (Scheme 104).



Scheme 104

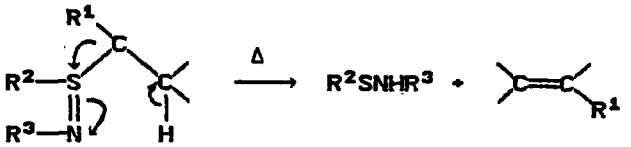
4.1.2. *Reactions Involving Conversion of the S=N Bond to an S^{II}=N or S^{IV}—N Bond*

4.1.2.1. *Rearrangement of Sulfimides to Sulfenamides* *N*-Substituted sulfimides containing an aryl group at the sulfur atom are subject to various facile sigmatropic rearrangements, therefore it is impossible to isolate them in many instances. One of the rearrangements of this type is the [2,3]-sigmatropic rearrangement consisting in allyl group migration from sulfur to nitrogen to yield *N*-substituted sulfenamides (Scheme 105).[290]



Scheme 105

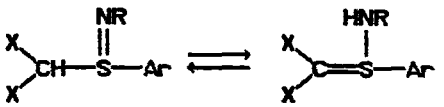
When heated, *S*-alkyl sulfimides containing β-hydrogen atoms undergo rearrangement of the Pummerer type to yield sulfimides and alkenes (Scheme 106).[66,291]



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

Scheme 106

4.1.2.2. *Formation of* S-*Aminosulfonium Ylides* *N*-Substituted sulfimides containing a mobile α-hydrogen atom can undergo [1,3]-sigmatropic rearrangement to form *S*-aminosulfonium ylides (Scheme 107).

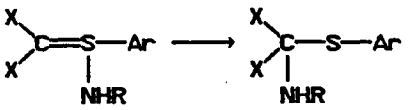


Scheme 107

The rearrangement is essentially a prototropic shift in the C—S—N moiety, *i.e.*, imino ylide tautomerism, and the possibility of existence of any form depends on the nature of the X and R groups.

In accordance with the main principles of acid-base prototropic equilibrium[292] the tautomeric equilibrium is the case when the dissociation constants of the two forms differ by no more than one to three orders of magnitude. If the difference between the dissociation constants is great the equilibrium shifts nearly completely towards the form with the lesser dissociation constant. If this criterion is applied to the C—S—N imino ylide tautomerism of *N*-substituted sulfimides with a mobile α-hydrogen atom it will be clear that the transformation of imine to ylide occurs only when the acidity of the CH-form (imine) becomes comparable to or greater than that of the NH-form (ylide). To make the CH-form acidity equal or greater than the NH-form acidity a strong electron-acceptor effect of the X groups is required. Therefore, formation of *S*-aminosulfonium ylides is observed[48,51–53,108] when strong electron acceptor groups such as PhCO, MeCO, CN, EtOCO, etc. are introduced as X. If X is a weak electron acceptor such as Ph,[293] the prototropic tautomeric equilibrium completely shifts towards the weakly acidic imine form, *i.e.* the [1,3]-sigmatropic rearrangement does not occur.

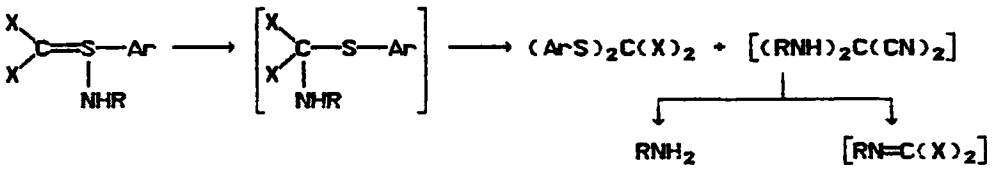
The stability of *S*-aminosulfonium ylides resulting from [1,3]-sigmatropic rearrangement of sulfimides is determined, to a greater extent, by the nature of the R groups on the nitrogen atom. A relatively high stability of *S*-aryl-*S*-(*t*-butylamino)- and *S*-aryl-*S*-(α-cyanoisopropylamino)sulfonium ylides has been reported[108] while *S*-aryl-*S*-(arenesulfonylamino)sulfonium ylides[51–53,108] are unstable and undergo further transformations due to the migration of the arenesulfonamido group to the carbon atom (Schemes 108 and 109).



X = PhCO, MeCO; Ar = 4-ClC$_6$H$_4$, 2-NO$_2$C$_6$H$_4$, 4-NO$_2$C$_6$H$_4$;

R = PhSO$_2$, 4-MeC$_6$H$_4$SO$_2$;

Scheme 108

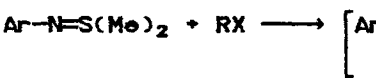


X = CN, EtOCO; Ar = 4-ClC$_6$H$_4$, 2-NO$_2$C$_6$H$_4$, 4-NO$_2$C$_6$H$_4$;

R = PhSO$_2$, 4-MeC$_6$H$_4$SO$_2$

Scheme 109

4.1.2.3. *Formation of Aminosulfonium Halides* *N*-Aryl sulfimides form unstable aminosulfonium halides in their reactions with alkylating or acylating agents (Scheme 110).[293]

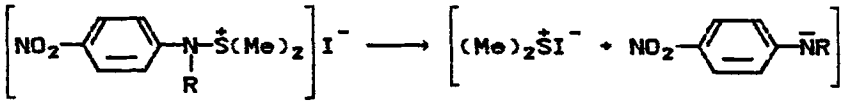


R = Me, X = I; R = EtOCO, X = Cl; R = MeCO, X = $MeCOO^-$;

Ar = *p*-$NO_2C_6H_4$, *p*-ClC_6H_4

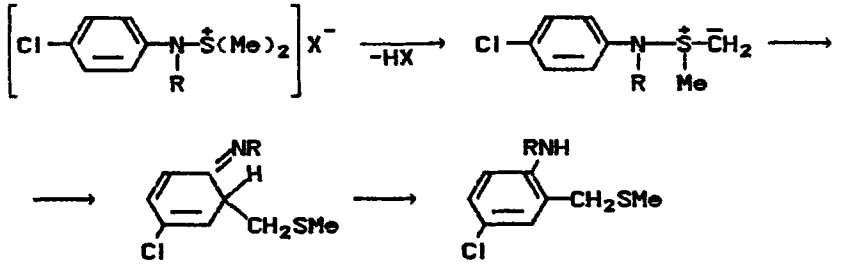
Scheme 110

Further transformations of such halides depend on the nature of the substituents of the aryl group and on the basicity of X. In the case of strong electron acceptor substituents (*e.g.* NO_2) and highly basic X^- an attack of X^- on the positively charged sulfur atom with subsequent S—N bond cleavage take place (Scheme 111).



Scheme 111

With weak electron acceptor or electron donor substituents X^- abstracts a proton from the *S*-methyl group to form an intermediate ylide which further undergoes intramolecular sigmatropic rearrangement resulting in an unstable cyclohexadiene derivative which is converted to a more stable benzene derivative (Scheme 112).

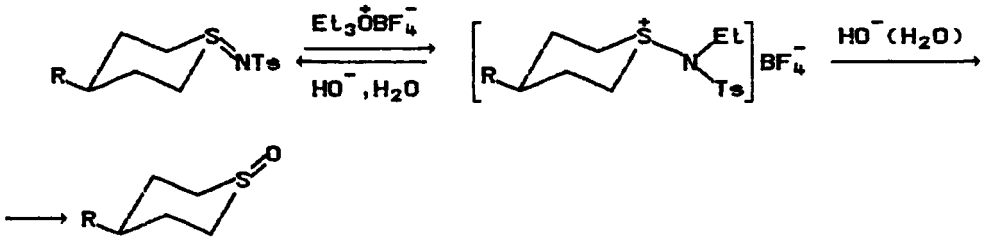


R = Me, X = I; R = MeCO, X = MeCOO; R = EtOCO, X = Cl

Scheme 112

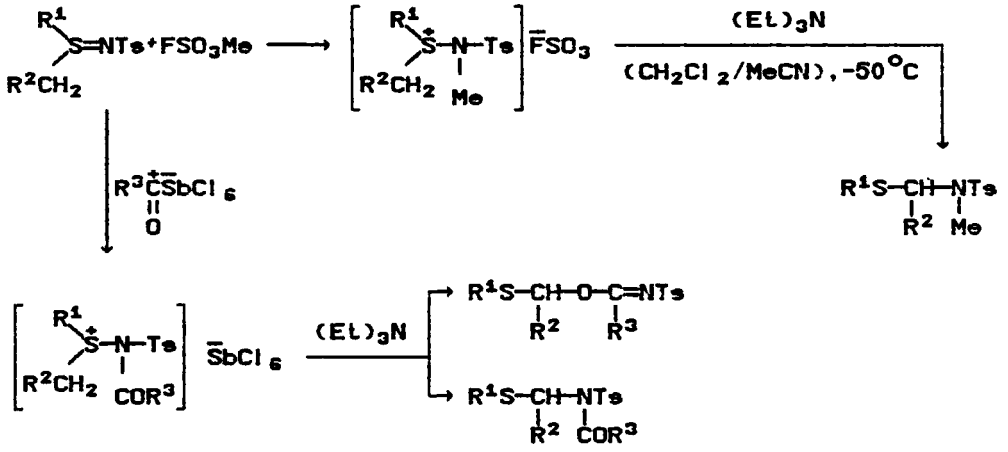
When one of the methyl groups on the sulfur atom is replaced by an ethyl or propyl group the proton is abstracted from the *S*-methyl group only, but in case of a benzyl group the proton is abstracted from the benzyl group only, which is correlated with a decrease of acidity in the series $PhCH_2S > MeS > AlkCH_2S$.

N-Arenesulfonyl sulfimides give aminosulfonium halides in reactions with highly active acylating and alkylating agents such as oxonium salts (*e.g.* $Et_3\overset{+}{O}BF_4^-$[291]), fluorosulfuric acid methyl ester,[294] and complexes of carboxylic acid chlorides with $SbCl_5$.[294] The aminosulfonium halides produced in this case are relatively stable and undergo further conversions under the action of mineral and organic bases only (Schemes 113 and 114).



R = *t*-Bu

Scheme 113



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

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

R^1 = Et, R^2 = H, R^3 = Me

Scheme 114

4.1.3. *Reactions with Complete Cleavage of the S=N Bond*

4.1.3.1. *Thermolysis and Photolysis of Sulfimides* The composition and nature of the products of the thermal decomposition of sulfimides are determined, as a rule, by their structure and the reaction conditions. The thermal destruction processes are often accompanied by various rearrangements which also favor the observed diversity of thermolysis products. Thus, the thermolysis of *N*-acyl-*S*,*S*-diphenyl sulfimides,[295] for example, is accompanied by rearrangement to a sulfide and an isocyanate (Scheme 115).

$$Ph_2SNCOR \xrightarrow{200^\circ C,\ 2h} RNCO + Ph_2S$$

$$R = PhCH_2,\ PhCH_2CH_2,\ 2,4,6\text{-}(Me)_3C_6H_2,\ Ph$$

Scheme 115

The thermolysis of *N*-(*o*-toluenesulfonyl)-*S*,*S*-dimethyl and -diphenyl sulfimide[296] at 300 °C in a nitrogen stream is accompanied by reduction reactions to give a mixture of products from which Me_2S, $(MeS)_2$, $(MeS)_2CH_2$, 4-$MeC_6H_4SO_2NH_2$, PhMe, $(4\text{-}MeC_6H_4S)_2$, 4-MeC_6H_4SSMe could be isolated. The thermolysis of heterocyclic sulfimides is often accompanied by ring expansion.[297] The primary products of sulfimide photolysis[298,299] are normally the starting sulfides and nitrenes which, depending on their structure and the reaction medium, afford various secondary products.

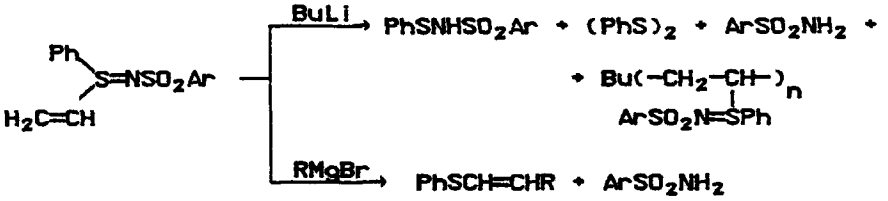
4.1.3.2. *Reduction of Sulfimides* Sulfimides are readily reduced by various reagents to yield the starting sulfides (Scheme 116).

$$R^1R^2S{=}NR^3 \xrightarrow{reduction} R^1SR^3 + R^3NH_2$$

$$R^1 = R^2 = Alk,\ Ar;\ R^3 = H,\ Ar,\ AlkSO_2,\ ArSO_2$$

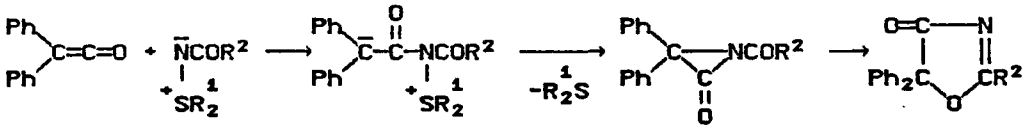
Scheme 116

Phosphorus pentasulfide,[277] titanium tetrachloride with zinc metal,[280] cysteine,[300] sodium iodide,[301] lithium alumohydride[302] and other reducing agents can be used as reducing agents. The reaction of *N*-arenesulfonyl-*S*-aryl-*S*-vinyl sulfimides with lithium- and magnesiumorganic compounds involves the reduction of these sulfimides (Scheme 117).[303]



Scheme 117

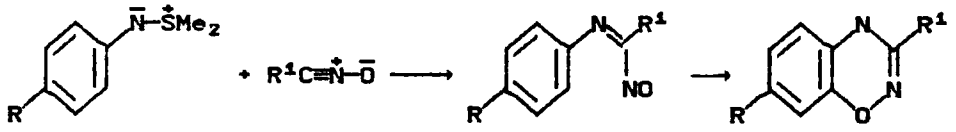
4.1.3.3. *Cycloadditions* The ylide character of the S=N bond in sulfimides makes it possible to use them in cycloaddition reactions with compounds containing activated double or triple bonds and systems with cumulated or conjugated double bonds.[304] The [4+2]-cycloaddition of *N*-substituted sulfimides with compounds containing activated C=C bonds has been studied.[304] The adducts formed in the reaction are cleaved to give highly reactive thionitroso compounds R—N=S (R = PhCO, EtOCO, $ArSO_2$). The adducts of the [2+2]-cycloaddition of sulfimides with carbon disulfide[275,293] are cleave to yield isothiocyanates, sulfides, and sulfur. Some cycloadditions involve only the nitrogen atom and the associated groups. These reactions are used for the synthesis of heterocyclic compounds. The reaction of *N*-acyl sulfimides with diphenylketene[305] is an example. The first step of this reaction is a nucleophilic attack of the sulfimide nitrogen atom on the electron-deficient carbon atom of the C=O group of diphenylketene, followed by cyclization of an intermediate dipolar compound to yield an unstable ethylenimine derivative rearranging to a more stable 1,3-oxazol-4-one derivative (Scheme 118).



R^1 = Me, Ph; R^2 = Me, CF_3, Ph, $PhCH_2$

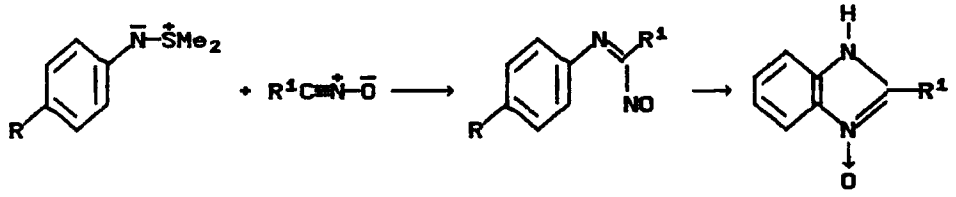
Scheme 118

1,2,4-Benzoxadiazines are reported[30] to be the products of the cycloaddition of *N*-aryl sulfimides to nitrile *N*-oxides (Scheme 119).



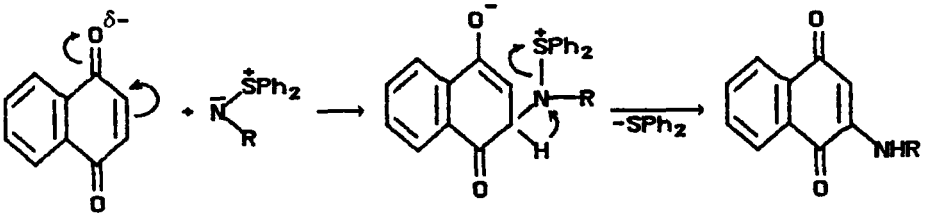
Scheme 119

However, according to Shinsaku *et al.*,[307] this cycloaddition involves the nitrile oxide nitrogen rather than the oxygen and leads to benzimidazole *N*-oxides (Scheme 120).



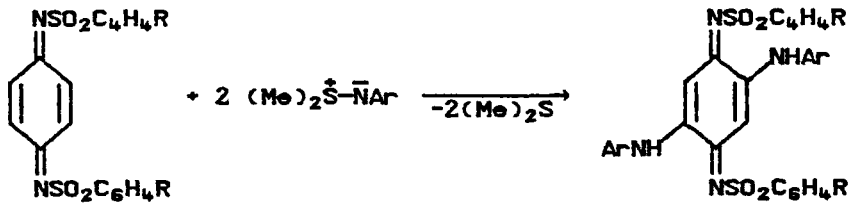
Scheme 120

4.1.3.4. *Addition to Quinoid Systems* The high nucleophilicity of the nitrogen of *N*-aryl sulfimides allows their use in nucleophilic additions to the nitrogen atom of the polar system of conjugated bonds of quinolines[308] and quinonimines.[309] The mechanism supposed involves nucleophilic attack of the sulfimide nitrogen on the terminal carbon atom of the conjugated bond system to yield an unstable betaine which converts to a more stable quinone or quinonimine derivative as a result of displacement by a neighboring acidic proton (Schemes 121 and 122).



R = $PhCH_2$

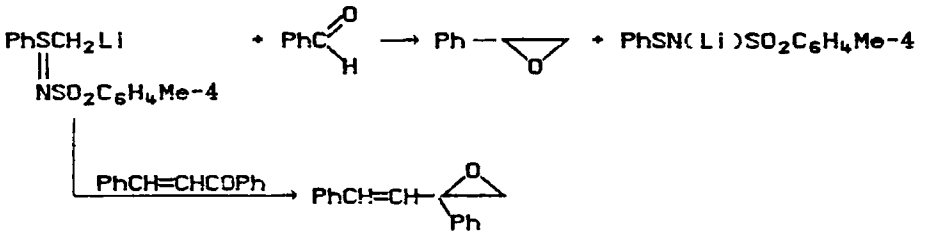
Scheme 121



R = H, 4-Me; Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-$NO_2C_6H_4$

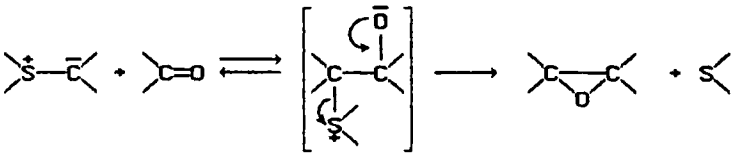
Scheme 122

4.1.3.5. *Transfer of Alkylidene Groups* The strong electron acceptor effect of the arylsulfonylimino group increases the acidity of the α-hydrogen atoms of the *S*-alkyl groups which facilitates their replacement by an alkali metal atom. The organometallic compounds so formed are used as nucleophilic reagents transferring an alkylidene groups to the electrophilic double bond (*e.g.*, C=O) to form a ring.[310] The leaving group the loss of which brings about the formation of the ring is a stable anion of an *N*-arenesulfonylsulfenamide which further favors this process (Scheme 123).



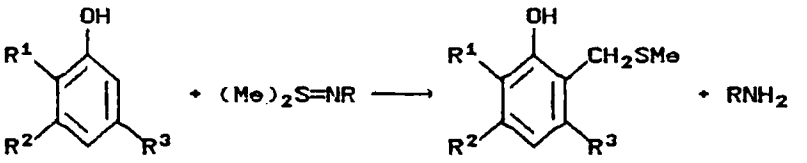
Scheme 123

The reaction is distinguished by its high stereoselectivity and if other *S*-alkyl sulfimides are used the 1,2-disubstituted oxiranes formed are predominantly of *trans*-structure.[311] By analogy with the mechanism of transfer of alkylidene groups from sulfur ylides to electrophilic double bonds[300] the mechanism of this reaction involves the formation of an intermediate betaine, followed by cyclization via a direct substitution at the carbon atom (Scheme 124).



Scheme 124

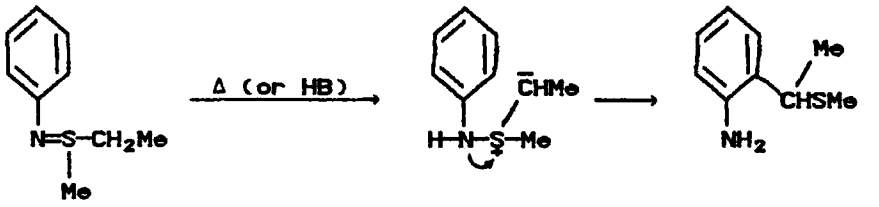
Use of *S*,*S*-dimethyl sulfimides for the introduction of the methylthiomethylene groups into the aromatic ring of phenols (Scheme 125) has been reported in the literature.[312]



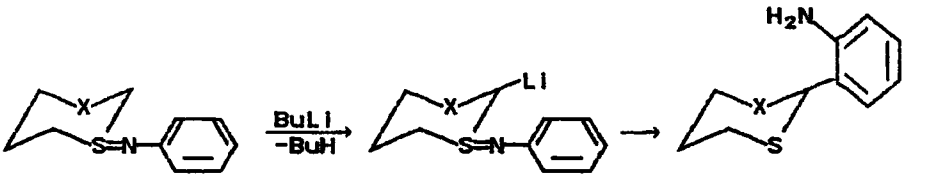
R^1 = Me, OMe; R^2 = H, Me; R^3 = H, Me; R = $ArSO_2$, 2,4-$(NO_2)_2C_6H_3$

Scheme 125

When heated[313] or treated with bases[314] or organolithium compounds[45] some *N*-aryl sulfimides undergo rearrangements of the Sommelet type (Schemes 126 and 127).[315]

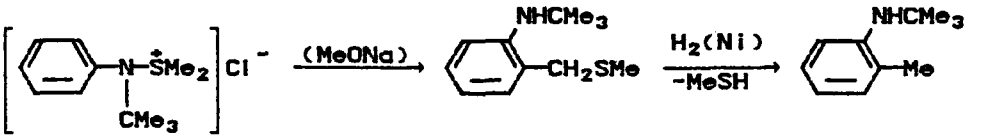


Scheme 126



Scheme 127

Gassman *et al.*[316] used a similar rearrangement of aminosulfonium halides for the ortho-alkylation of arylamines (Scheme 128).



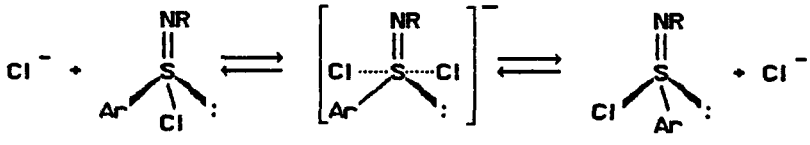
Scheme 128

4.2. *Reactions of Iminosulfinic Acid Halides*

Iminosulfinic acid halides are highly reactive towards nucleophilic reagents. Depending on the nucleophile and the reaction conditions reactions of iminosulfinic acid halides with nucleophiles can proceed in two alternative directions: with replacement of halide from the tetracoordinate sulfur by a nucleophile by an S_N2 mechanism or with reduction of the halide to a sulfenamide. In the latter case the nucleophile is halogenated by the halide.

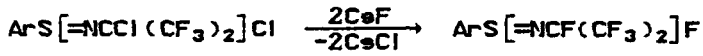
4.2.1. *Halide anions* When iminosulfinic acid halides react with a source of halide anions the halogen atom attached to the tetracoordinate sulfur is replaced another halogen atom. Tertiary amine hydrochlorides, BCl_3, PCl_5, $SiCl_4$, potassium, sodium and cesium fluorides and other metal halides are used as the source of the halide anions. In the reaction of *N*-(α-chloralkyl)iminosulfinic acid chlorides with triethylammonium chloride in methylene chloride[256] it is only the sulfur

atom which is attacked by chloride; the reaction occurs by an S_{N2} mechanism with inversion at the sulfur atom (Scheme 129).



Scheme 129

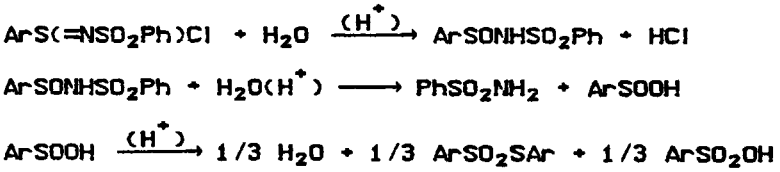
If cesium fluoride is used chlorine atoms are replaced by fluorine at both the sulfur atom and the carbon atom at a practically equal rate (Scheme 130).



Scheme 130

The replacement of the fluorine atom with chlorine in *N*-substituted trifluoroethanoyliminosulfinic acid fluorides can be achieved by heating with boron trichloride, phosphorus pentachloride, or silicon tetrachloride.[133,134]

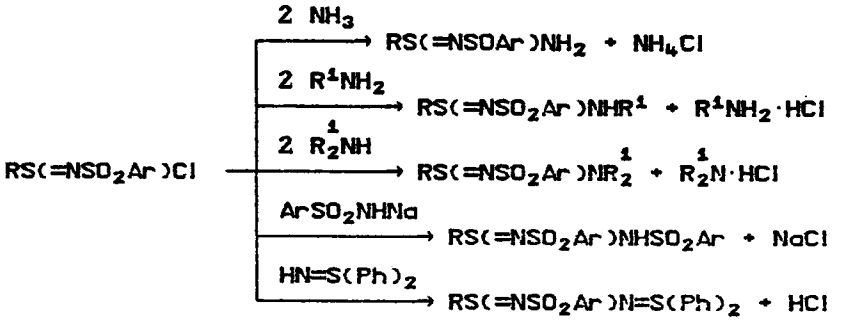
4.2.2. *With* O-*Nucleophiles* In the presence of water iminosulfinic acid chlorides are readily hydrolyzed yielding various products the nature of which depends on the structure of the starting material and on the reaction conditions. The hydrolysis of *N*-arenesulfonylareneiminosulfinic acid chlorides in the presence of mineral acids[317] first yields *N*-arenesulfonylamides of arenesulfinic acids which are cleaved to arenesulfonamides and arenesulfinic acids. The latter disproportionate in acidic media to give arenethiosulfonic acid esters and arenesulfonic acids (Scheme 131).



Scheme 131

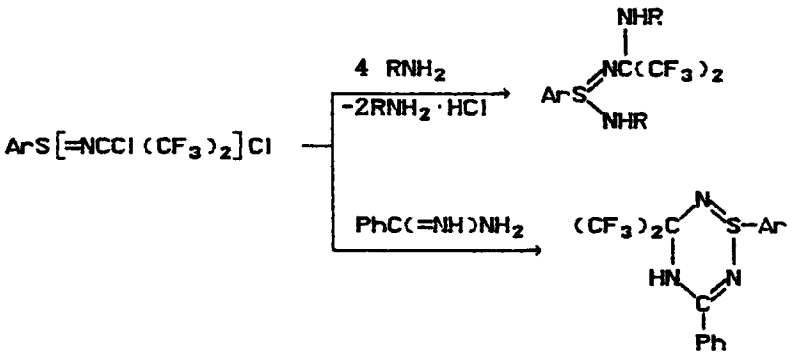
In the presence of alkali the hydrolysis of *N*-arenesulfonylareneiminosulfinic acid chlorides leads to arenesulfinic acid *N*-arenesulfonylamides.[317] As already mentioned, reactions of iminosulfinic acid chlorides with alcohols or alkoxides give iminosulfinic acid esters.

4.2.3. *With* N-*Nucleophiles* With ammonia and its derivatives *N*-arenesulfonyliminosulfinic acid chlorides form iminosulfinic acid amides (Scheme 132).[117,281,318]



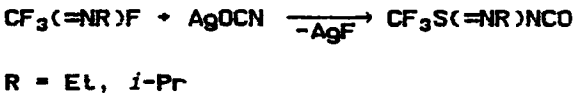
Scheme 132

In the reactions of *N*-(α-chloralkyl)areneiminosulfinic acid chlorides with *N*-nucleophiles both electrophilic centers[129,256] are involved (Scheme 133).



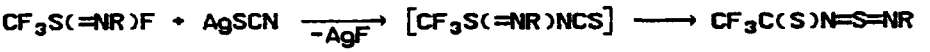
Scheme 133

As shown,[135] *N*-substituted trifluoromethanoyliminosulfinic acid fluorides react with silver cyanate to yield the corresponding isocyanates (Scheme 134).



Scheme 134

When silver thiocyanate is used the isothiocyanates formed rearrange to sulfur diimides (Scheme 135).[135]

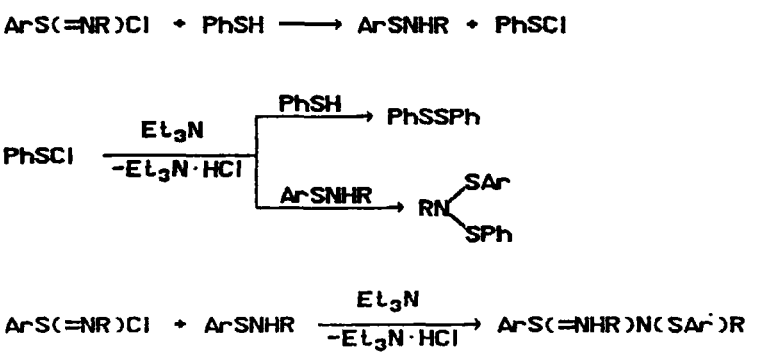


Scheme 135

4.2.4. *With* S-*Nucleophiles* Depending on the conditions, reactions of *N*-substituted areneiminosulfinic acid chlorides with arenethiols can proceed in two alternative directions. In the absence of bases, sulfenyl chlorides and *N*-substituted sulfenamides are formed (Scheme 136).[156,171,172]

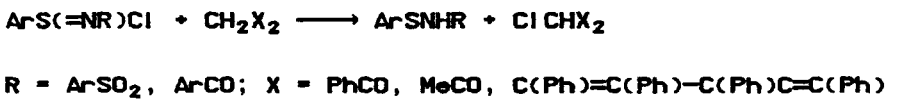
Scheme 136

In the presence of triethylamine, diaryl disulfides, *N*,*N*-bis(arylthio)amides and *N*-arenesulfenyl-*N*,*N'*-diacylsulfinamidines (Scheme 137) are formed.



Scheme 137

4.2.5. *With* C-*Nucleophiles* The reactions of *N*-substituted iminosulfinic acid chlorides with CH-acids also proceed in two alternative directions. In the absence of bases, the chlorides are reduced to *N*-substituted sulfenamides and the CH-acids are chlorinated (Scheme 138).[319,320]



Scheme 138

In the presence of triethylamine, CH-acids are acylated by the chlorides to form *N*-substituted sulfimides (Scheme 24).

4.3. *Reactions of Iminosulfinic Acid Amides*

4.3.1. *Acidic Properties* *N,N'*-Disubstituted iminosulfinic acid amides are monobasic NH-acids the pK_a of which varies over a wide range with the nature of the groups at the nitrogen and the sulfur (Table 7).

The nature of the groups at the nitrogen and sulfur atoms governs the acidic properties of iminosulfinic acid amides. Thus, the replacement of an arenesulfonyl group at one of the nitrogen atoms of *N,N'*-bis(arenesulfonyl)alkanesulfinamidines (pk_a 2.84–3.33 by acyl) (pK_a 5.99) or aryl (pK_a 10.60–10.62) brings about a significant reduction of the acidity of these compounds.

As seen from the pK_a values of *N*-acyl-*N'*-arenesulfonylsulfinamidines, the nature of the substituents of the arenesulfonyl group has little effect on the acidic properties of these compounds which is probably due to poor transmission of inductive effects through the sulfonyl group. A stronger effect on the properties of these compounds is produced by the substituents on the aryl group and especially those directly bound to the tetravalent sulfur atom which is also confirmed by correlation analysis data. The correlation between the pK_a and the Hammett σ-constants of the arenesulfonyl substituents ($\rho = -0.1$) has been determined for a series of *N,N'*-bis(arenesulfonyl)propanesulfinamidines $PrS(=NSO_2C_6H_4R)NHSO_2C_6H_4R$ (R = H, 4-Me, 4-NO_2, 4-Br, 4-Cl) and between the pK_a and the Taft σ^*-constants of the alkanesulfinamidine substituents ($\rho^* = +2.58$)[170] for a

TABLE 7 pK_a Values of Iminosulfinic Acid Amides[117,170,189]

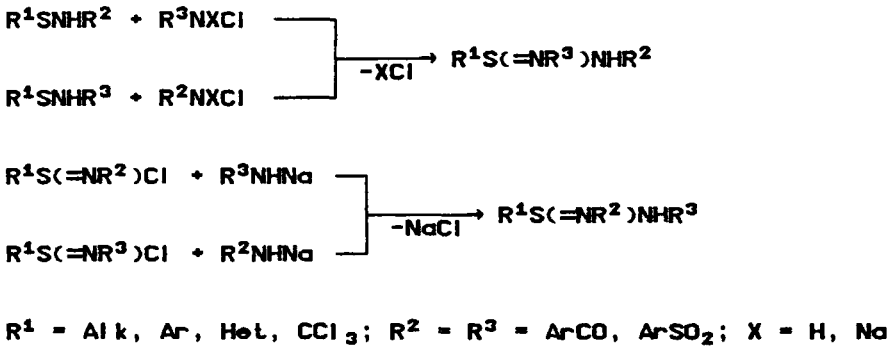
Amide	pK_a	Solvent
$CCl_3S(=NSO_2Ph)NHCOC_6H_4NO_2$-4	2.74	a
i-$PrS(=NSO_2Ph)NHSO_2Ph$	2.84	b
$CF_2ClS(=NSO_2Ph)NHCOPh$	2.88	a
$CCl_3S(=NSO_2Ph)NHCOC_6H_4Cl$-4	2.89	a
$CFCl_2S(=NSO_2Ph)NHCOPh$	2.91	a
$C_5H_{11}S(=NSO_2Ph)NHSO_2Ph$	2.91	b
$CCl_3S(=NSO_2C_6H_4Cl$-4$)NHCOPh$	2.92	a
n-$PrS(=NSO_2C_6H_4NO_2$-3$)NHSO_2C_6H_4NO_2$-3	2.93	b
n-$PrS(=NSO_2C_6H_4Br$-4$)NHSO_2C_6H_4Br$-4	2.94	b
$CCl_3S(=NSO_2Ph)NHCOPh$	2.95	a
$CCl_3S(=NSO_2C_6H_4Me$-4$)NHCOPh$	2.96	a
n-$PrS(=NSO_2C_6H_4Cl$-4$)NHSO_2C_6H_4Cl$-4	2.96	b
n-$BuS(=NSO_2Ph)NHSO_2Ph$	2.98	b
$CCl_2S(=NSO_2Ph)NHCOC_6H_4Me$-4	2.99	a
i-$BuS(=NSO_2Ph)NHSO_2Ph$	3.02	b
n-$PrS(=NSO_2Ph)NHSO_2Ph$	3.04	b
n-$PrS(=NSO_2C_6H_4Me$-4$)NHSO_2C_6H_4Me$-4	3.05	b
$CCl_3S(=NSO_2Ph)NHCOC_6H_4OMe$-4	3.08	a
$MeS(=NSO_2Ph)NHSO_2Ph$	3.33	b
$ClCH_2S(=NSO_2Ph)NHCOPh$	4.75	a
$MeS(=NSO_2Ph)NHCOPh$	5.99	a
n-$BuS(=NSO_2C_6H_4NO_2$-3$)NHC_6H_4Me$-4	10.60	c
$C_5H_{11}S(=NSO_2Ph)NHPh$	10.62	c

a) 50% acetone aqueous; b) 1% methanol aqueous; c) 50% methanol aqueous.

series of *N*,*N*′-bis(benzenesulfonyl)alkanesulfinamidines $RS(=NSO_2Ph)NHSO_2Ph$ (R = Me, Pr, Bu, C_5H_{11}, *i*-Pr, *i*-Bu). A correlation between the pK_a values of *N*-aroyl-*N*′-benzenesulfonyltrichloromethanesulfinamidines $CCl_3S(=NSO_2Ph)NHCOC_6H_4R$ (R = H, 4-Me, 4-MeO, 4-Cl, 4-NO_2) and the Hammett σ-constants of the aryl substituents ($\rho = -0.2669$)[189] has been established. A correlation between the pK_a and the Taft σ*-constants of the sulfinamidine substituents ($\rho^* = -1.1604$) has been found for a series of *N*-benzoyl-*N*′-benzenesulfonylsulfinamidines $RS(=NSO_2Ph)NHCOPh$ (R = Me, $ClCH_2$, CCl_3, $CClF_2$, CCl_2F).

N,*N*′-Bis(arenesulfonyl)sulfinamidines in their reactions with $NaHCO_3$, $Hg(NO_3)_2$ and $AgNO_3$ form the corresponding sodium, mercury and silver salts, respectively.[117,146]

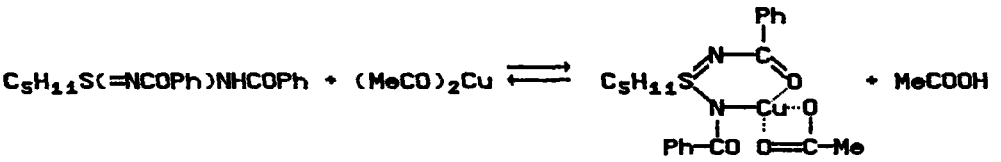
4.3.2. *Tautomerism of Iminosulfinic Acid Amides* *N*,*N*′-Disubstituted iminosulfinic acid amides containing arenesulfonyl and acyl groups as substituents show a tendency to prototropic tautomerism in the N—S—N moiety, the presence of which was established[22,117,183,192] as a result of the transformations shown below (Scheme 139).



Scheme 139

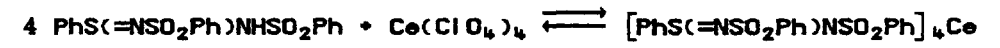
It has been demonstrated by IR and NMR spectroscopy that the tautomeric equilibrium is always shifted towards a more thermodynamically advantageous form of lower acidity. The value of the prototropic tautomeric equilibrium constant is dependent on the nature of the groups at the nitrogen atoms and, more correctly, on the difference between the electronegativities of these groups, an increase in which increases the prototropic tautomeric equilibrium constant.

4.3.3. *Formation of Complex Compounds* The complex forming ability of iminosulfinic acid amides has not been investigated properly though, as shown by the literature data,[17,321] these compounds can be of interest as potential complexing agents. It has been established[321] that, in its reaction with copper acetate, *N*,*N*′-dibenzoylpentanesulfinamidine forms a bright-green complex with an absorption maximum at 690 nm (Scheme 140).



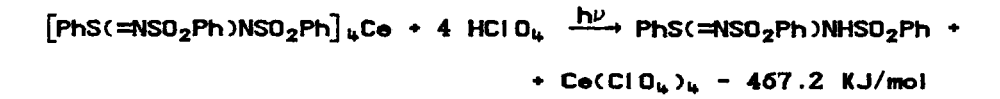
Scheme 140

Upon dissolution of *N,N'*-bis(benzenesulfonyl)benzenesulfinamidine in aqueous $Ce(ClO_4)_4$ the formation of an unstable cerium complex was observed (Scheme 141).[17]



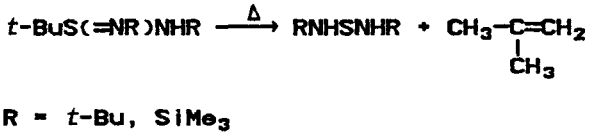
Scheme 141

Ultraviolet irradiation of the complex in the wavelength range 1800–2600 Å leads to its decomposition with a high endothermal effect (Scheme 142).



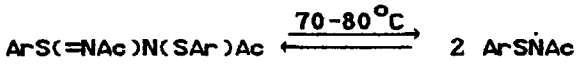
Scheme 142

4.3.4. *Thermolysis* The thermal stability of iminosulfinic acid amides depends on the nature of the groups at the nitrogen atom as shown[322] in the thermolysis of *N,N'*-disubstituted amides of *t*-butyliminosulfinic acid *t*-BuS(=NR)NHR (R = *t*-Bu, $SiMe_3$, $SnMe_3$). The thermolysis of amides containing *t*-butyl and trimethylsilyl groups proceeds relatively readily at 40–60 °C to form diaminosulfanes and isobutene (Scheme 143) while the thermolysis of amides containing trimethylstannyl groups at the nitrogen atoms proceeds at above 110 °C to yield a mixture of products.



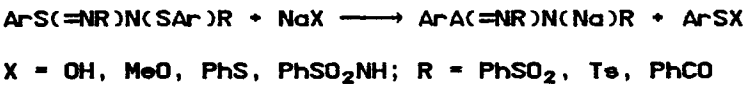
Scheme 143

Iminosulfinic acid amides containing arenesulfonyl and acyl groups at the nitrogen atoms possess a higher thermal stability. It has been established[146,171,172] that heating of *N*-arenesulfenyl-*N,N'*-diacylarenesulfinamidines in inert organic solvents brings about the formation of stable *N*-arenesulfenylacyliminyl radicals (Scheme 144).

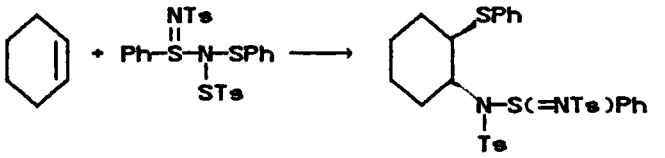


Scheme 144

4.3.5. *Reactions with Nucleophilic Reagents* The high stability of the S—N bond in *N*-arenesulfenyl-*N*,*N*′-bis(arenesulfonyl)arenesulfinamidines allows the use of these compounds as sulfenylating agents in reactions involving nucleophilic reagents (Scheme 145)[146,171,172] as well as in the aminosulfenylation of cycloalkenes (Scheme 146).[323]

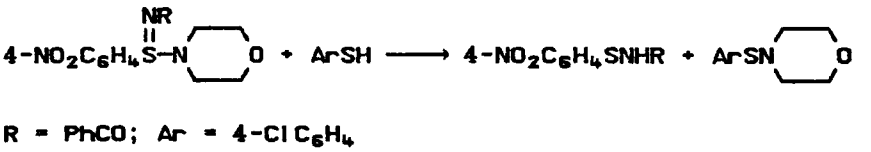


Scheme 145



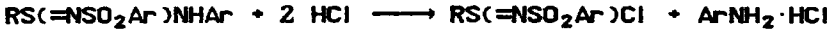
Scheme 146

The cleavage of some iminosulfinic acid amides in the presence of arenethiols is accompanied by reduction at the sulfur atom (Scheme 147).[324]



Scheme 147

4.3.6. *Reactions with Electrophilic Reagents* The reaction of *N*-aryl-*N*′-arenesulfonylalkanesulfinamidines with hydrogen chloride in benzene gives *N*-arenesulfonylalkaneiminosulfinic acid chlorides (Scheme 148).[117]

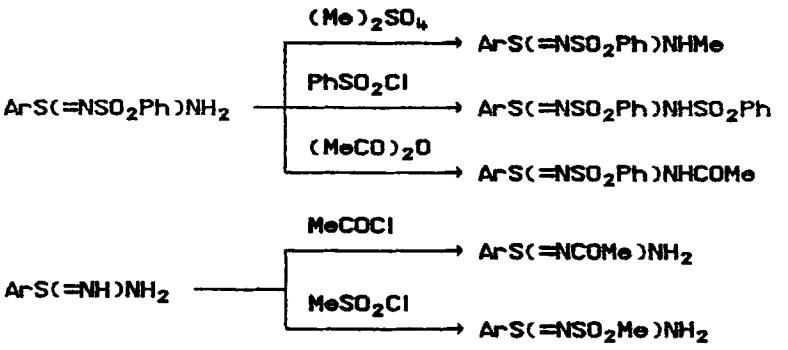


Scheme 148

N,N'-Diacylarenesulfinamidines react with hydrogen chloride to yield bis(acylamino)sulfonium chlorides cleaving, when heated, to *N*-acyliminosulfinic acid chlorides and carboxamides (Scheme 149).[111]

Scheme 149

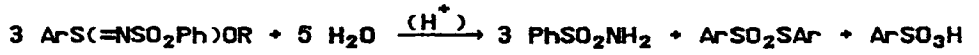
Alkylation and acylation of iminosulfinic acid amides proceed regiospecifically at the more nucleophilic nitrogen atom (Scheme 150).[181,322]



Scheme 150

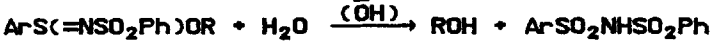
4.4. *Reactions of Iminosulfinic Acid Esters*

Iminosulfinic acid esters are the least studied of all tetravalent sulfur imino compounds, evidently due to their low reactivity. They are resistent to the action of oxidants, do not change when heated with water, and are only slowly hydrolyzed by dilute hydrochloric acid to give a mixture of various products (Scheme 151).[21]



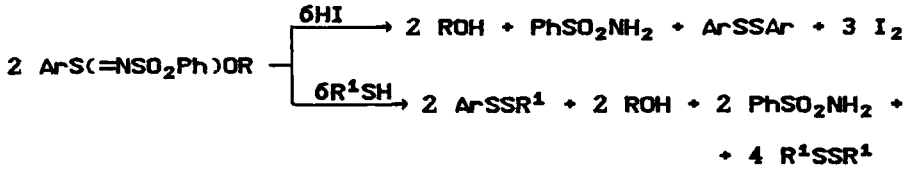
Scheme 151

Hydrolysis of *N*-arenesulfonyliminosulfinic acid esters in alkaline media proceeds with formation of alcohols and *N*-arenesulfonylarenesulfinamides (Scheme 152).



Scheme 152

In the presence of hydriodic acid[198] as well as arenethiols[324] the cleavage of some iminosulfinic acid esters is accompanied by reduction of the tetravalent sulfur to the divalent state (Scheme 153).



Scheme 153

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