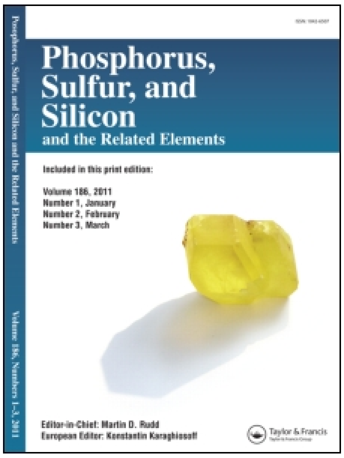

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Á. Kucsman[a]; I. Kapovits[a]
[a] Department of Organic Chemistry, Eötvös University, Budapest, Hungary

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STRUCTURE, STEREOCHEMISTRY, AND MECHANISM OF FORMATION OF *N*-ACYLSULFILIMINES†

by

Á. Kucsman and I. Kapovits

Department of Organic Chemistry, Eötvös University, Budapest, Hungary

CONTENTS

ABSTRACT

The methods for the preparation of sulfilimines are summarized, and the stereochemistry and electronic structure of *N*-acylsulfilimines are discussed. Sulfilimines have a non-planar structure, but the S^{IV}–N bond character cannot be determined from their resolvability. *N*-Sulfonylsulfilimines ($RR'SNSO_2Q$) contain a delocalized $S^{IV}NS^{VI}$ $d\pi$ bond system, the $S^{IV}N$ and $S^{VI}n$ bonds are of intermediate bond order. $S^{IV}–CH_3$ hyperconjugation causes strong bond shortening. An asymmetric conformation of a sulfilimine containing two identical S^{IV} substituents was found in the crystalline state which could be accounted for theoretically. The rotation of the SN bond is not restricted in solution. The structure of *N*-carboacylsulfilimines (RR'SNCOQ) is strongly polar due to the strong NCO conjugation, and the instability of these compounds can be ascribed to the polar structure. The reaction between thioethers and chloramine-T is a nucleophilic substitution; the rate of the reaction is influenced by the nucleophilic character of the thioether sulfur atom. Thioether carboxylic acids are usually oxidized by chloramine-T and only give a sulfilimine if the carboxyl group is fixed sufficiently distant from the sulfur atom. The formation of sulfilimines from an optically active sulfoxide by the action of a sulfonamide (or *N*-sulfinylsulfonamide) proceeds *via* a trigonal bipyramidal intermediate with complete inversion. The intermediate of the sulfilimine synthesis starting from arylsulfonyl azides is a sulfonyl imene.

I. METHODS OF PREPARATION

The sulfilimines were discovered by Raper[1] (1917) in connection with his investigations on mustard gas, which reacts with chloramine-T by elimination of sodium chloride under formation of a readily crystallizing sulfilimine:

$$(ClCH_2CH_2)_2S + TsNCl^{\ominus}Na^{\oplus} \xrightarrow{-NaCl} (ClCH_2CH_2)_2SNTs$$

Later investigations by Mann and Pope,[2] started in 1922, revealed that this reaction is rather general: thioethers other than mustard gas react in the same manner, and chloramine-T can be replaced with sodium salts of other *N*-halosulfonamides or *N*-haloamides. The Mann-Pope reaction might be then be generalized as:

$$RR'S + AcNCl^{\ominus}Na^{\oplus} \xrightarrow{-NaCl} RR'SNAc$$

Water, methanol, acetone, dioxane, or mixtures of these may be used as solvents. The reaction proceeds easily, in many cases even without application of external heat.

Quite a number of various *N*-acylsulfilimines have been prepared so far as shown in Table I.

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TABLE I

N-Acylsulfilimines (RR'SNAc)

Acyl	Reference	R and R'	Reference
benzenesulfonyl	3,4	alkyl	2,14
toluenesulfonyl	2	alkenyl	9,15-17
4-acetaminobenzenesulfonyl	5	haloalkyl	2,18-22
4-nitrobenzenesulfonyl	6	hydroxyalkyl	15,23
4-halogenbenzenesulfonyl	7,8	alkoxyalkyl	24,25
2-nitrotoluenesulfonyl	9	acyloxyalkyl	26
naphthalene-1-sulfonyl	9	alkylaminoalkyl	27
4-azobenzenesulfonyl	10	oxoalkyl	18
benzylsulfonyl	11	carboxyalkyl	28-30
acetyl	12	cycloalkyl	29
dihalogenacetyl	13	aryl	5,31,32
propionyl	12	aralkyl	2,33
benzoyl	12	haloaryl	32,34
		alkoxyaryl	32
		nitroaryl	32
		acetaminoaryl	5
		carboxyaryl	30,35,36
		cyanoaryl	37
		heterocyclic	5,30,38

$ArSO_2NCl^{\ominus}Na^{\oplus}$ compounds react with sulfur dichloride to form *S,S*-dichloro-*N*-arylsulfonylsulfilimines.[39] An analogous reaction occurs if $S(NR_2)_2$ is used instead of SCl_2.[8,40] The halogen atoms of *S*-chloro derivatives can easily be replaced by alkylamino or acylamino groups.[40]

The sulfilimines, obtained without difficulty from thioethers and suitable compounds of chloramine-T type ($XC_6H_4SO_2NCl^{\ominus}Na^{\oplus}$, X = H, *p*-Me, *p*-$NO_2$, *p*-Br), crystallize so readily that sulfilimine formation has found widespread use for separation and identification of thioethers. The parent thioether can be regenerated smoothly by the reduction of the sulfilimines.[9,31] Various methods were employed for identification of the sulfilimines: melting point determination,[14,6] X-ray diffraction,[41] ir spectroscopy,[11,13,42-44] uv spectroscopy,[45,46] nmr spectroscopy,[43,47-49] analysis of optical rotatory dispersion,[50] mass spectrometry,[43] and chromatography.[6,16,50-54]

Another known method[55] for the preparation of the sulfilimines is the condensation of sulfoxides with suitable amides in warm acetic anhyride or in hot chloroform solution with phosphor pentoxide (the reaction occurs already in the cold in the presence of triethylamine[50]):

$$RR'SO + AcNH_2 \xrightarrow{-H_2O} RR'SNAc$$

This reaction described by Tarbell and Weaver[55] has been used, however, only in a few cases (R, R' = Et, Bu, tetramethylene, Ph, *p*-MeC_6H_4; Ac = Ts, $COCHCl_2$, $COCCl_3$ or $COCHBr_2$[13]). Aromatic sulfoxides do not react with haloacetamides.[55,13]

King[56] reported in 1960 that the reaction of *p*-toluenesulfonyl isocyanate and dimethyl sulfoxide gives the sulfilimine in good yield:

$$Me_2SO + TsNCO \xrightarrow{-CO_2} Me_2SNTs$$

Sulfuryl diisocyanate,[57] dichloroacetyl isocyanate, and trichloroacetyl isocyanate[58,49] react analogously.

The process of Schulz and Kresze[59] for the preparation of sulfilimines is based on the reaction of *N*-sulfinylsulfonamides and sulfoxides:

$$RR'SO + QSO_2NSO \xrightarrow{-SO_2} RR'SNSO_2Q$$

If Q = *p*-MeC_6H_4, the reaction proceeds readily with aliphatic sulfoxides, but if Q = Me, the reaction also occurs with methyl phenyl sulfoxide or diphenyl sulfoxide. The procedure can be extended to *N*-sulfinylhaloacetamides ($CHCl_2CONSO$, CCl_3CONSO); these yield the appropriate *N*-halogenacetylsulfilimine with dimethyl sulfoxide.[49]

According to investigations of Horner and Christmann,[60] sulfilimines are formed from some sulfonyl azides in the presence of dimethyl sulfide by action of uv light:

$$Me_2S + ArSO_2N_3 \xrightarrow{-N_2} Me_2SNSO_2Ar$$

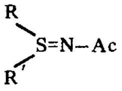
$$Ar = p\text{-}MeC_6H_4,\ p\text{-}MeOC_6H_4,\ p\text{-}O_2NC_6H_4$$

Recently some sulfilimines different from *N*-acylsulfilimines discussed previously have been prepared by special methods. Sulfilimines having free NH groups (R_2SNH, R = Me, Et, *p*-$MeOC_6H_4$) are labile compounds which can be acylated to give *N*-acylsulfilimines.[61-63] It has been shown that some sulfilimines containing fluorine atoms are very stable (F_2SNQ; Q = *e.g.*, Ph, CF_3, $PhCF_2$[43] or Me, Et[64,65]); if Q = Ph, fluorine atoms could be exchanged with methoxy or phenyl groups. Similarly the chlorine atoms of ArClSNAc (Ac = SO_2Ar, CO_2R) and Cl_2SNAr-type compounds are reactive and can be substituted by alkoxy or alkylamino groups.[66-68] Also known are RR′SNAc sulfilimines in which the R′ substituent is an acylamino or alkylamino group.[69-72] Compounds of the general formula $[R_2SNSR_2]^{\oplus}$-$Cl^{\ominus}$ [73,74] and $S(NSO_2Ar)_2$[75] deserve to be mentioned because the structure is related to that of the sulfilimines.

II. STRUCTURE

Sulfilimines are the substituted derivatives of the hypothetical "sulfilimine" (H_2SNH). They can also be derived from the sulfoxides by substituting an imino or substituted imino group for the oxygen atom. Most of the known and stable sulfilimines contain an *N*-acyl group.

In 1922 Mann and Pope,[2] employing classical valence theory, formulated the structure of the sulfilimines with a SN double bond (**1**). In 1927, Phillips and his coworkers[35] suggested the structural formula 2 based upon the octet principle with a semipolar SN bond:



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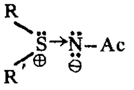

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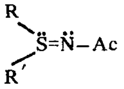

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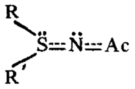
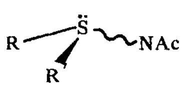


4

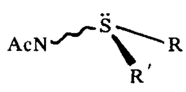
Since the octet principle does not apply to all bond forms of sulfur and theory allows for a SN double bond (dπ bond), formula 3 was suggested[76] in 1953 as this could be brought into agreement with the known experimental facts. In *N*-acylsulfilimines, however, the SN bond is not isolated but can interact with the electron system of the *N*-acyl group as expressed by formula **4**.[77]

In 1924, Mann and Pope[78] postulated stereoisomerism from formula 1 because of the double-bond character of the SN link (and not on account of the asymmetry of the sulfur atom). They compared the sulfilimines to resolvable hydrazone and oxime types, where dissymmetry arises from the valence orientation of the double-bonded nitrogen atom. Having produced, however, no experimental evidence in favor of their view, their somewhat laconic and not very clear discussion of the subject passed into oblivion.

Phillips and his coworkers[35,36] in 1927-1928 succeeded in resolving two sulfilimines (R = Me or Et; R′ = *m*-$HO_2CC_6H_4$; Ac = Ts) into optical antipodes. These experimental results gave unquestionable evidence that the sulfilimines (similar to sulfoxides[79] and sulfinic esters[80]) have non-planar configuration (**5a** and **5b**, without indication of the SN bond character):



5a



5b

Phillips interpreted the optical isomerism of the sulfilimines on the basis of formula **2**, but beyond that he regarded the resolvability as independent experimental evidence of SN (in case of sulfoxides and sulfinic esters: SO) semipolar bond character (**5a** and **5b** with S–N bond).

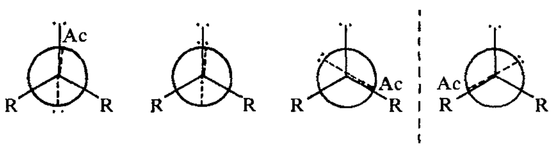
Kucsman[76] showed in 1953 that the stereochemical proof of Phillips concerning the SN (and SO) bond character is wrong in principle as it is based on the unconditional validity of the octet principle and supposes *a priori* the analogous spatial arrangement of analogous carbon and sulfur compounds. The optical isomerism of sulfilimines (and in analogy to this that of the sulfoxides and sulfinic acid esters) can also be interpreted using formula 3.

It was elucidated by Jaffé's theoretical investigations[81] in 1954 that a dπ bond can also belong to a tetrahedral central atom. We are therefore theoretically justified to assume that in compounds of type $RR'\ddot{S}Q$ (Q = NAc or O) the central sulfur atom is surrounded by the single-bonded R and R′ substituents, the double-bonded Q is substituent and the lone electron pair approximately according to a tetrahedral orientation. This gives the possibility of the occurrence of enantiomorphous spatial arrangements (**5a** and **5b** with $S{=}N$ bond).[77]

In spite of considerations mentioned above, the incorrect stereochemical "evidence" given by Phillips as to the SN and SO bond-characters seemed so convincing that authors of several well-known textbooks (Fieser and Fieser,[82] Karrer,[83] Müller,[84] Klages[85]) even nowadays quote the SO and SN bonds of the sulfoxides and sulfilimines as typical examples of the semipolar bond, in some cases referring to the optical activity as additional evidence. Other treatises use the formulas with semipolar bonds without comments.[86,87] Nevertheless, the stereochemical treatment of sulfur compounds taking into account the SO and SN $d\pi$ bonds is found more and more in textbook literature (*e.g.*, Bruckner,[88] Staab,[89] Fodor,[90] Roberts and Caserio[91]).

The structural problem of sulfilimines is not limited to the determination of the SN bond character. Namely, the nitrogen atom of *N*-acylsulfilimines is—in contrast to the oxygen atom of sulfoxides—not a terminal atom, but it is bonded to an acyl group which is more or less prone to conjugation. Therefore, we must not only decide whether the SN bond has double-bond character and how it is influenced by the R and R′ substituents of the sulfur atom (such problems occurred, *e.g.*, during the structural investigations of sulfoxides) but also what effect the acyl group exerts on the bond system. The presence of the *N*-acyl group has also stereochemical consequences: if the nitrogen atom is in a $d\pi$ bond, it is open to question whether the acyl group bound to it is in a fixed spatial arrangement as the Q group in compounds containing the $>C{=}\ddot{N}{-}Q$ partial structure. If the SN rotation is restricted, the appearance of stereoisomerism is also conceivable, even in the case of symmetrically substituted $R_2\ddot{S}{=}\ddot{N}{-}Ac$ sulfilimines because of the spatially fixed position of the *N*-acyl group.[77] Some idealized possibilities of stereoisomerism are shown in Figure I (the sulfur and nitrogen atoms are to be imagined in the center). Structures **6** and **7** are symmetric, whereas the enantiomeric structures, **8a** and **8b**, are asymmetric.

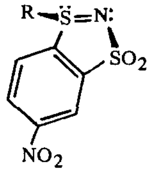
The stereoisomerism (optical or *cis-trans* isomerism) of sulfilimines of the R_2SNTs-type, based on restricted rotation of the SN bond, could not be proved by resolution or isomerisation.[27] So the stereochemical methods did not give evidence referring to the SN double-bond character.



6 *trans* 7 *cis* 8a *asym.* 8b *asym.*

FIGURE I

It may be mentioned that in the cyclic sulfilimines, **9**, prepared by Wagner[42] the sulfur atom of the acyl group is a member of a ring and is therefore fixed. Configurationally the cyclic sulfilimines are of type **8**.[77]



9

The results of the physical investigations which appeared since 1964 constitute a significant extension of our knowledge concerning *N*-acylsulfilimines.

In the ir spectra of *N*-sulfonylsulfilimines ($RR'SNSO_2Q$) the most characteristic part is the 1300-900 cm^{-1} region. Three high intensity bands always appear here at 1300-1270, 1150-1100, and 1020-935 cm^{-1}.[16,42,11] The first two bands belong to the SO_2 group whereas the third can be assigned to the stretching vibrations of the $S^{IV}N$ or more probably the $S^{IV}NS^{VI}$ grouping.[11,92] The correctness of this assignment can be proved experimentally. The band appearing at 974 cm^{-1} in the spectrum of *S,S*-diallyl-*N*-*p*-tolylsulfonylsulfilimine cannot be found in the spectrum of *N*-allyl-*N*-allylthio-*p*-toluenesulfonamide which is formed from the first-named compound by spontaneous isomerization (S → N allyl migration[9]). Since the ν_{SNS} frequency (1020-935 cm^{-1}) is smaller in the case of sulfilimines than the value observed for the ν_{SO} vibration of sulfoxides (1092-1012 cm^{-1}), the strength of the SN bond is less than that of the SO bond. It is certain, however, that the SN bond is much stronger than a single bond.

According to experience the frequency and integrated intensity of the ν_{SNS} and ν_{SO_2} bands in the spectra of *N*-sulfonylsulfilimines vary slightly with the character of the R, R′, and Q groups. The following theoretical deductions could be made from this fact.[11,92]

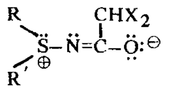
N-sulfonylsulfilimines contain a relatively strong $S^{IV}N$ $d\pi$ bond, but it cannot be decided definitely on the basis of ir data whether this group is isolated (**3**) or part of a delocalized SNS $d\pi$ bond system (**4**).

A weak conjugative interaction exists between the $S^{IV}N$ bond and the aromatic ring(s) attached to the S^{IV} atom. This is shown *inter alia* by the fact that the ν_{SNS} frequency of *S,S*-diphenylsulfilimines is always smaller than that of the analogous *S,S*-diethyl derivatives ($\Delta\nu_{SNS}$: 5-18 cm^{-1}), and the integrated intensity is enhanced at the same time. No similar phenomenon is observed in the case of sulfoxides.[93]

A further difference between the fine structure of sulfilimines and sulfoxides also deserves interest. Whereas dimethyl sulfoxide is characterized in the sulfoxide series by an extremely high ν_{SO} frequency and integrated intensity, the situation in the sulfilimine series is just the opposite. Sulfilimines of S^{IV}-methyl type have surprisingly low ν_{SNS} frequencies and integrated intensities compared to the analogous S^{IV}-ethyl derivatives ($\Delta\nu_{SNS}$: 16-33 cm^{-1}). This may be attributed to CH_3-S^{IV} hyperconjugation which may enhance the electron density on the sulfur atom. Bond-length data treated subsequently are in accordance with this concept.

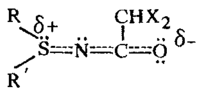
The $S^{VI}O$ and $S^{VI}N$ bonds of *N*-sulfonylsulfilimines do not conjugate with each other, the lowering of the ν_{SO_2} frequencies of sulfilimines compared with those of sulfonamides and sulfones ($\Delta\bar{\nu}_{SO_2}$: 38-50 and 10-20 cm^{-1}) can also be interpreted by an inductive effect. The Q group also exerts its effect on the SO_2 group inductively. It is interesting, however, that the influence of the Q group is different on the SO and SN bonds belonging to the same S^{VI} atom. This can be deduced from the fact that although ν_{SO_2} slightly increased ($\Delta\bar{\nu}_{SO_2}$: 15-18 cm^{-1}) in connection with the Q = aliphatic → aromatic change, ν_{SNS} slightly decreases ($\Delta\nu_{SNS}$: 13-18 cm^{-1}). The two different effects of the Q group are probably connected with the steric conditions caused by the tetrahedral central sulfur atom. The orientation of the nitrogen atom and the aryl group bound to the S^{VI} sulfur atom, which exert the least influence on the electron system of the SO_2 group ("case II of conjugation" according to Koch and Moffitt[94]), necessarily gives some possibility for the interaction between the aromatic ring and the nitrogen atom through the sulfur atom.

N-Carboacylsulfilimines (RR′SNCOQ; Q = *e.g.*, $CHCl_2$, $CHBr_2$, CCl_3) have contrary to *N*-sulfonylsulfilimines a very weak SN dπ bond; at the same time the carbonyl group is very polar (ν_{SN}: 800-825 cm^{-1}, ν_{CO}: 1608-1615 cm^{-1}), which can be expressed by the limiting structure, **10**, or formula **11**.[13]



$$\overset{R}{\underset{R'}{}}\overset{\oplus}{\ddot{S}}-\ddot{N}=\overset{CHX_2}{C}-\ddot{O}:^{\ominus}$$

10

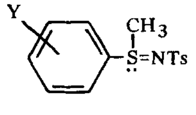


$$\overset{R}{\underset{R'}{}}\overset{\delta+}{\ddot{S}}\text{┄}\ddot{N}\text{┄}\overset{CHX_2}{C}\text{┄}\ddot{O}^{\,\delta-}$$

11

The instability and reactivity of some *N*-carboacylsulfilimines (*e.g.*, Q = Me) is evidently connected with the strong polar structure which is somewhat decreased in the case of the above-mentioned compounds by the strong –I effect of the halomethyl groups.

Uv spectroscopic investigations[46] showed that the SN group is a chromophore; the absorption band, however, shows a hypsochromic shift relative to the analogous band of the sulfoxides. This is accounted for with the polarity of the SN bond which is higher than that of the SO bond. According to uv spectra the S^{IV} sulfur atom in *S*-methyl-*S*-arylsulfilimines has acceptor character. This manifests itself pregnantly if a *p*-OMe or *p*-OH group occurs on the aromatic ring (*e.g.*, **12**; Y = *p*-OMe or *p*-OH).



12

The acceptor character of the S^{IV} sulfur atom in the $CH_3S^{IV}NTs$ group bound to an aryl group is also proved by Hammett σ constants:

σ_m: 0.67; σ_p: 0.64 (**12**; Y = *m*-CO_2H and *p*-CO_2H)
σ'_m: 0.82; σ'_p: 0.99 (**12**; Y = *m*-OH and *p*-OH)[95]

The more thorough analysis of the bond system and conformation of *N*-sulfonylsulfilimines was made possible by the X-ray diffraction investigation of *S,S*-dimethyl-*N*-methylsulfonylsulfilimine (Me_2SNSO_2Me).[96,97] The spatial structure of this compound including bond-length and bond-angle data is shown in Figure II.

Bond-length data of SN show that the p orbital of the sp^2 hybridized nitrogen atom combines with the d orbitals of the S^{IV} and S^{VI} sulfur atoms in such a way that strong dπ bonds of intermediate bond order are formed with both sulfur atoms. So the sulfilimine contains a delocalized $S^{IV}NS^{VI}$ dπ system according

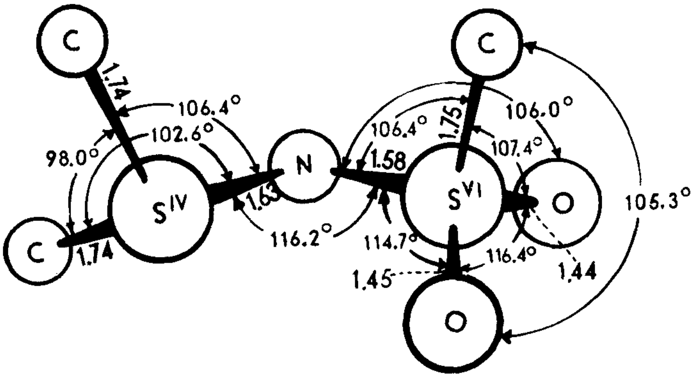


FIGURE II

Bond Lengths and Bond Angles of
S,S-Dimethyl-*N*-methylsulfonylsulfilimine

to IV ($S^{IV}N$ 1.63, S^{VI} 1.58 Å, theoretically S–N 1.76, S=N 1.52 Å). In comparing the SN bond lengths of the sulfilimine with each other, it has to be taken into account that the electronegativity and atomic radius of the sulfur atom in S^{IV} valence state differ from those of the S^{VI} valence state, and $S^{IV}X$ bonds are usually 0.03–0.05 Å longer than analogous $S^{VI}X$ bonds. The average value of the SO bond lengths in the sulfilimine (1.445 Å)* coincides with those of the sulfones. The strength of the $S^{VI}O$ dπ bonds in the SO_2 group is not weakened by the strong $S^{VI}N$ dπ bond belonging to the same sulfur atom and, at the same time, the formation of a strong $S^{VI}N$ dπ bond is not hindered by the presence of the SO_2 group. Thus, in the $NS^{VI}O_2$ moiety the S^{VI} sulfur atom is to be considered a center of a cumulated dπ bond system. It is worth mentioning that all this cannot be satisfactorily interpreted by Jaffé's theory[81] relating to the conjugative interaction of dπ bonds belonging to a tetrahedral central sulfur atom.†

The $S^{IV}C$ bonds in the sulfilimine are remarkably short (1.74 Å).* This value is the shortest one found so far for $S^{IV}C$ (*e.g.*, C–S in dimethyl sulfoxide 1.81 Å). The significant bond shortening can perhaps be accounted for by a hyperconjugation-like interaction between the electron systems of methyl groups and the sulfur atom. (*cf.* ir data[11]). The valence angles of the S^{IV} sulfur atom are almost the same in the sulfilimine as in dimethyl sulfoxide.

A theoretical interpretation of the sulfilimine conformation can be based on the examination of how the sulfur atoms are oriented to the sp^2 hybridized nitrogen atom. Figure III shows that the spatial arrangement around the S^{VI} atom corresponds to "case II of conjugation" according to Koch and Moffitt.[94] As a consequence of this arrangement minimum interaction exists between the electron system of the SO_2 group and the p orbital of the nitrogen atom. The conformation of the molecular moiety around the S^{IV} atom is determined by the *trans* position of the lone electron pairs belonging to the sulfur and nitrogen atoms (Figure IV).

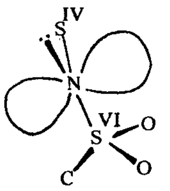


FIGURE III

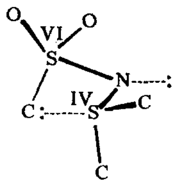


FIGURE IV

It can be seen in Figure II that the actual conformation of the sulfilimine is asymmetric and, according to the position of the *N*-acyl group relative to the S^{IV} pyramid, of *trans* character. It follows from crystallographic data of the sulfilimine that the crystal-lattice contains not only the one antipode of the asymmetric molecule shown in Figure II, but also its mirror image, which means that sulfilimine (despite two identical *S*-substituents) appears as a racemate in the crystalline state.

According to nmr investigations[49] the structural position of the two S^{IV}-methyl groups in *S,S*-dimethyl-*N*-*p*-tolylsulfonylsulfilimine relative to the $NSO_2C_6H_4Me$ moiety of the molecule does not differ from each other since the peak due to the S^{IV}-methyl groups in the spectrum does not show splitting even at –45°. It is therefore probable that the asymmetric conformation of the sulfilimine is not fixed by the SN dπ bond in solution.

The absolute configuration of an *S*-asymmetric sulfilimine became known from the investigations of Day and Cram[50] in 1965: (–)-*S*-methyl-*S*-*p*-tolyl-*N*-*p*-tolylsulfonylsulfilimine has (*S*)-configuration.

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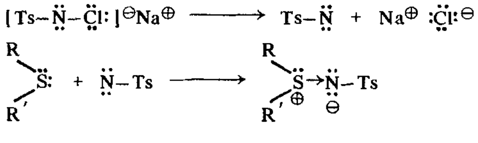
* *According to Cruickshank's private communication–if the librational correction is taken into account–the* $S^{IV}C$ *bond lengths can be estimated to be 1.78 and 1.80 Å whereas the* $S^{VI}O$ *bond lengths are 1.47 Å. This correction does not influence the theoretical conclusions outlined above.*

† *According to Jaffé: "... around a tetrahedral central atom M, introduction of a second dπ-bonded group reduces the double-bond character of the already existing dπ-bond. Two unlike groups enter into competition, with the result that the stronger dπ-bonding group will approach maximum bonding at the expense of the weaker bonding group. Hence conjugation will appear greatly reduced."*

III. MECHANISM

The first concept of the reaction mechanism between thioethers and chloramine-T (Mann-Pope reaction) is due to Phillips and his coworkers[35]. They suggest that the reaction proceeds *via* two steps:

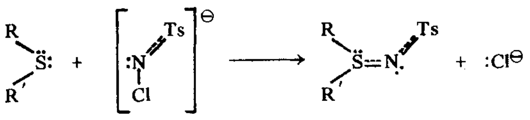


$$[Ts-\ddot{N}-\ddot{Cl}:]^{\ominus}Na^{\oplus} \longrightarrow Ts-\ddot{N} + Na^{\oplus}\,:\ddot{Cl}:^{\ominus}$$

$$RR'\ddot{S}: + \ddot{N}-Ts \longrightarrow RR'\overset{\oplus}{S}\rightarrow\overset{\ominus}{\ddot{N}}-Ts$$

This explanation seems to be formalistic as the decomposition of chloramine-T to yield an imene intermediate under the reaction conditions is not probable, and there is no experimental proof on this point.

It is more in accord with experimental facts, if the formation of the sulfilimines is regarded as nucleophilic substitution with the thioether as nucleophilic.[32]



The well-known ability of dialkyl sulfides to form sulfilimines can be accounted for by the donor character of the alkyl groups.

Methyl phenyl sulfide and its substituted derivatives ($CH_3SC_6H_4X$, X = H, OMe, $CO_2^{\ominus}$, Br, NO_2) also give sulfilimine easily, independently of the donor or acceptor character of the group X. Hence the exchange of one single alkyl group with an aryl group does not change the nucleophilic character of the thioether decisively as far as the given reaction is concerned.

Diphenyl sulfide, however, reacts only sluggishly with chloramine-T, and the reactivity of its substituted derivatives ($XC_6H_4SC_6H_4X$) depends on the character of the substituents. In the presence of groups with +M effect (*e.g.*, OMe) sulfilimines are again formed readily. If, on the other hand, the aromatic ring is substituted by a group with –M effect (*e.g.*, NO_2), no sulfilimine formation can be detected.

The qualitative conclusions[32] mentioned above are borne out by quantitative kinetic measurements done by Dell'Erba and Spinelli[98] on substituted methyl phenyl sulfides ($MeSC_6H_4X$; X = *p*-MeO, *p*-Me, *m*-Me, H, *p*-Cl, *m*-Cl, *m*-NO_2, *p*-NO_2). The substituent of the aryl group influences the reaction rate according to its donor or acceptor character; a relatively higher electron density on the thioether sulfur atom is favourable to the reaction, and the change in rate constant follows the Hammett relationship with a negative ρ.

The reaction of thioethers with chloramine-T is not limited exclusively to sulfilimine formation. It has been observed previously that if the reaction is carried out in a medium containing water, sulfilimine formation is accompanied to some degree by oxidation of the thioether.[14]

$$RR'S + TsNCl^{\ominus} \xrightarrow[\text{formation}]{\text{sulfilimine}} RR'SNTs + Cl^{\ominus}$$

$$RR'S + TsNCl^{\ominus} + H_2O \xrightarrow{\text{oxidation}} RR'SO + TsNH_2 + Cl^{\ominus}$$

In the latter side-reaction the thioether is oxidized to the sulfoxide by chloramine-T, which in turn is reduced to *p*-toluenesulfonamide. This reaction comes definitely to the fore with thioether carboxylic acids. Tananger[28] and Weibull[29] have shown that numerous $RSCH_2CO_2H$ (R = aliphatic or aromatic) type thioethers are susceptible to oxidation and not to the formation of sulfilimines. These authors state that thioether carboxylic acids also form sulfilimines primarily which, however, on account of their instability, undergo hydrolysis to the corresponding sulfoxide and *p*-toluenesulfonamide.

On the other hand, it could be shown that the reactions leading to the formation of the sulfilimine and the sulfoxide do not occur consecutively but concurrently, so that sulfoxides are not formed by the hydrolysis of the sulfilimines.[30] The ratio of the two competitive reactions will be determined by the structure of the thioether carboxylic acids and by the solvent.

Parallel experiments with chloramine-T and several different thioether carboxylic acids proved that the oxidizability of the thioether carboxylic acids (in water at pH 7) is not decisively influenced by their aromatic or aliphatic character or by the –I and –M effect of the carboxylic group. The tendency for oxidation depends primarily on steric factors.[30] In carboxylic acids which are prone to oxidation the carboxyl group is fixed near to the sulfur atom or can approach it by rotation. Sulfilimines, on the other hand, are formed from such carboxylic acids in which the carboxyl group is fixed far from the sulfur atom.

So the *m*- and *p*-carboxy substituted derivatives of methyl phenyl sulfide and diphenyl sulfide ($MeSC_6H_4CO_2H$, $HO_2CC_6H_4CO_2H$) give sulfilimines whereas sulfoxides are formed from the *o*-carboxy derivatives. Compounds containing the *o*-CH_2CO_2H group instead of the *o*-CO_2H group are also oxidized. Tetrahydrothiophene carboxylic acids undergo oxidation almost quantitatively. In the carboxy-tetrahydrothiopyrane series oxidizability decreases according to the 2, 3, or 4 position of the carboxyl group. The equatorial position of this group in 3-carboxy and 4-carboxy derivatives is favorable for the reaction yielding the sulfilimine (this could be obtained with a 65% yield from the 4-carboxy derivative).

It can be assumed that the spatial proximity of the carboxyl (carboxylate) group in thioether carboxylic acids enhances the electron-donating ability of the thioether sulfur atom which evidently favors the oxidation reaction. On the other hand, it must also be presumed that the reaction leading to the formation of the sulfilimine is less sensitive to the change of the nucleophilic character of the sulfur atom. The shift in the ratio of the competitive reactions can also be due to the shielding effect of the carboxyl group adjacent to the sulfur atom, and this influences sulfilimine formation more than oxidation.

Benes[99] investigated the mechanism of the reaction between chloramine-B and mustard gas using kinetic methods. According to his opinion the formation of the sulfilimine and sulfoxide occurs *via* a series of consecutive and simultaneous reactions which can be described by the following scheme ($Ac = PhSO_2$, $R = CH_2CH_2Cl$):

$$AcNCl^{\ominus} + H_2O \rightleftharpoons AcNHCl + OH^{\ominus}$$

$$AcNHCl + R_2S \xrightarrow{k} AcNH^{\ominus} + R_2SCl^{\oplus}$$

$$R_2SCl^{\oplus} + AcNH^{\ominus} \longrightarrow R_2\overset{\oplus}{S}-\overset{\ominus}{N}Ac + H^{\oplus} + Cl^{\ominus}$$

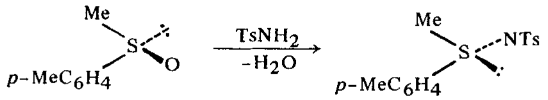
$$R_2SCl^{\oplus} + H_2O \longrightarrow R_2SO + 2H^{\oplus} + Cl^{\ominus}$$

The author does not mention the reaction $AcNH^{\ominus} + H^{\oplus} \rightarrow AcNH_2$, but it is evident that this process is also part of the series.

In the scheme detailed above, the neutral AcNHCl intermediate formed in the hydrolysis equilibrium of the chloramine-B chlorinates the thioether in the rate-determining step. The $R_2SCl^{\oplus}$ intermediate so formed is converted in fast processes, by the nucleophilic attack of the $AcNH^{\ominus}$ intermediate or a water molecule, to the sulfilimine or the sulfoxide.

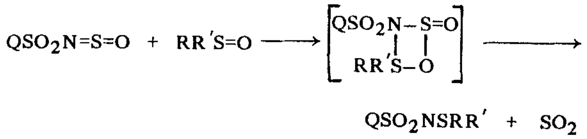
Although this mechanism explains some characteristics of the reaction (the thioether is the nucleophilic reagent, the sulfoxide is not the hydrolysis product of the sulfilimine), it cannot be accepted without reservations since the experimental data are insufficient and the calculations contain some unallowable simplifications.

The formation of sulfilimines from sulfoxides (Tarbell-Weaver condensation) is a nucleophilic substitution according to Day and Cram.[50] The reaction is accompanied with complete inversion if the sulfoxide has asymmetric structure. So the (dextrorotatory) methyl *p*-tolyl (*R*)-sulfoxide is converted to (laevorotatory) *S*-methyl-*S*-*p*-tolyl-*N*-*p*-tolylsulfonyl-(*S*)-sulfilimine by *p*-toluenesulfonamide:



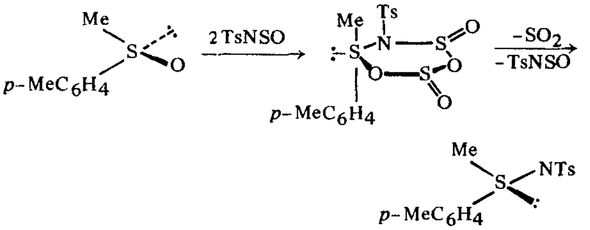
The authors are of the opinion that the intermediate of the reaction has a trigonal bipyramidal structure in which the entering and leaving groups occupy a radial —not axial—position.

Schulz and Kresze[59] suppose that the transformation of *N*-sulfinylsulfonamides and sulfoxides to sulfilimines is a four-centered reaction proceeding through a cyclic intermediate:*



$$QSO_2N{=}S{=}O + RR'S{=}O \longrightarrow \left[\begin{array}{l} QSO_2N-S{=}O \\ \quad\;\; | \quad\;\; | \\ \quad RR'S-O \end{array}\right] \longrightarrow QSO_2NSRR' + SO_2$$

Day and Cram[50] showed that the synthesis starting from an asymmetric sulfoxide is accompanied by complete inversion. *S*-Methyl-*S*-*p*-tolyl-*N*-*p*-tolylsulfonyl-(*S*)-sulfilimine is also formed from methyl *p*-tolyl (*R*)-sulfoxide and *N*-sulfinyl-*p*-toluenesulfonamide. In the reaction sulfur dioxide is liberated, and thus the entering and leaving groups must be coupled in a ring system. The authors suggest that in the cyclic intermediate the orientation of the various groups around the sulfur atom is trigonal bipyramidal, the entering and leaving groups are in radial positions, and two molecules of *N*-sulfinylsulfonamide participate in the reaction.



The method of Horner and Christmann[60] for the preparation of *N*-sulfonylsulfilimines is also of theoretical interest. Arylsulfonyl azides decompose on warming and irradiation by uv light with the formation of sulfonyl imene having an electron sextet. This electrophilic intermediate becomes stable by formation of a sulfilimine in the presence of a thioether as a donor.

$$Ar{-}SO_2{-}N_3 \xrightarrow[-N_2]{h\nu} Ar{-}SO_2{-}\ddot{\underset{..}{N}} \xrightarrow{Me_2\ddot{S}:} Ar{-}SO_2{-}\ddot{N}{=}\ddot{S}Me_2$$

It is worth mentioning that a similar final step was postulated earlier by Phillips[35] in connection with the Mann-Pope condensation.

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* *King[56] gave an analogous interpretation of the reaction of p-toluenesulfonyl isocyanate and dimethyl sulfoxide where carbon dioxide is split off.*

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