The Chemistry of Sulfilimines

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Contents

I. Introduction

Sulfur–carbon ylides have proved to be important reagents in organic synthesis, particularly in reactions involving intramolecular rearrangement and intermolecular attack on substrates bearing an electrophilic carbon atom.[1] In recent years there has been increasing interest in developing a comparable chemistry of sulfur–nitrogen ylides. This review deals with one group of such ylides, represented by the general formula **1**, in which R^1 and R^2 are carbon substituents.

$$R^1R^2\overset{+}{S}-\overset{-}{N}R^3$$

1

These ylides are named as sulfilimines in *Chemical Abstracts* but as sulfimides according to IUPAC rules;[2] the name "iminosulfuranes" is also commonly used in current literature. The relationship of sulfilimines to other sulfur ylides, sulfoxides, and sulfones is as shown. A consideration of the relative electronegativities of the atoms involved leads to the prediction that the properties of sulfilimines should be intermediate between those of sulfonium ylides and of sulfoxides. They should also be similar in properties to the corresponding sulfoximines[3] but more reactive, just as the sulfonium ylides are more reactive than the corresponding oxosulfonium ylides.

$R^1R^2\overset{+}{S}-\overset{-}{C}R^3R^4$	$R^1R^2\overset{+}{S}-\overset{-}{N}R^3$	$R^1R^2\overset{+}{S}-\overset{-}{O}$
sulfonium ylides	sulfilimines	sulfoxides
$R^1R^2\overset{+}{S}O-\overset{-}{C}R^3R^4$	$R^1R^2\overset{+}{S}O-\overset{-}{N}R^3$	$R^1R^2SO_2$
oxosulfonium ylides	sulfoximines	sulfones

These generalizations seem to be borne out in terms of the structure, stability, and reactions of the sulfilimines which have been investigated so far.

The review is organized so as to provide a comparative survey of different types of sulfilimines; thus, general properties and general types of reactions are discussed. The tables in section II provide access to information on individual compounds. We have aimed to cover the literature to mid-1976, and to include in the tables all sulfilimines known at that time, with the exception of *N*-sulfonyl derivatives, for which only representative examples are listed. Structures of type **1** in which either of the groups R^1 or R^2 is attached to sulfur through a heteroatom are not correctly classed as sulfilimines, although they are often named as such; the chemistry of these compounds is included separately, in the form of a brief survey, in section VI.

Several earlier reviews[4] have dealt with aspects of sulfilimine chemistry.

II. Methods of Preparation

A. Reaction of Sulfides with *N*-Halo Compounds

The reaction of sulfides with chloramine-T and salts of other *N*-chloroarenesulfonamides was the first method to be discovered for preparing sulfilimines, and is still the method of choice for preparing most arenesulfonylsulfilimines. A report by Raper[5] in 1917 described the formation of a crystalline compound from the reaction of mustard gas with chloramine-T, and in 1921 Nicolet and Willard[6] obtained a crystalline derivative from diethyl sulfide and chloramine-T, to which a sulfilimine structure was tentatively assigned. Several sulfilimines were prepared in the same way by Mann and Pope[7] in 1922; since then the reaction has been widely used as a means of preparing crystalline derivatives of sulfides for characterization purposes. Sulfides can be regenerated from the sulfilimines by a variety of methods (section IV.F).

TABLE I. Representative *N*-Sulfonyl Substituted Sulfilimines, $R^1R^2S^+-\bar{N}SO_2R^3$

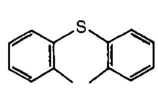
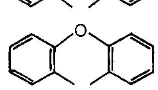
R^1	R^2	R^3	Mp, °C	Yield, %	Method[a]	Ref
Me	Me	Me	122–123	61	E	33
Me	Ph	Me	124–126	46	E	33
Ph	Ph	Me	91.5–92	38	E	33
Me	Me	CCl_3	174–176	43	E	*b*
Me	Me	CF_3	37–40	68	E	*c*
			29–30	85	E	108
Me	Me	Et_2N	47.5–48.5	64	B	13b
Me	Me	$(CH_2)_5N$	99.5–100.5	75	B	13b
Me	Me	$PhCH_2$	147–148	70	C	25
Ph	Ph	$PhCH_2$	136	31	A	94
$PhCH_2$	$PhCH_2$	$PhCH_2$	146	34	A	94
$PhCH_2$	$PhCH_2$	2-Thienyl	136		A	*d*
Me	Me	Ph	129–131	80	C	21
				50	B	*e*
			124–126	78	F	52
					F	42a
Me	Et	Ph	92–94		A	*f*
Me	Ph	Ph	87.5–88	59	A	112
Me	Me	*p*-MeC_6H_4	158–159	82	E	33
			157–158	87	E	30
			157–158	47	C	30
			154–156	73	F	50c
			157–157.5	90	A	10b
			158–159	77	C	25
			161–162		B	13a
			157–158	36	F	52
			160–160.5		H	63
				58	I	68
			156–158	26	H	56
Me	Et	*p*-MeC_6H_4	133		A	7
Me	*n*-Pr	*p*-MeC_6H_4	104–105		A	*g*
Me	*i*-Pr	*p*-MeC_6H_4	116–117		A	*g*, *h*
Me	*n*-Bu	*p*-MeC_6H_4	89–90.5	70	A	158a,*h*
Me	Ph	*p*-MeC_6H_4	132	65	A	*i*
Me	Ph	*p*-MeC_6H_4	129–130	90	A	10b
			131–132	66	H	56
Me	*m*-ClC_6H_4	*p*-MeC_6H_4	133.5–134.5	47	A	112
Me	*p*-$MeOC_6H_4$	*p*-MeC_6H_4	145	53	A	*i*
Me	*p*-$O_2NC_6H_4$	*p*-MeC_6H_4	159–160	56	A	*i*
CH_2Cl	CH_2Cl	*p*-MeC_6H_4	101–102		A	*j*
$CH_2{=}CH$	$CH_2{=}CH$	*p*-MeC_6H_4	91–93		A	*k*
Et	Et	*p*-MeC_6H_4	144	26	H	63
			142–143.5	59	H	56
			144–145	83	E	33
$-(CH_2)_4-$		*p*-MeC_6H_4	135–136	58	E	33
$-(CH_2)_5-$		*p*-MeC_6H_4	148.5–149		A	*h*
			147–148	65	H	56
$-(CH_2)_3SCH_2-$		*p*-MeC_6H_4	164–165	60	A	*l*
$-(CH_2)_2CHBu^t(CH_2)_2-$		*p*-MeC_6H_4	187–188	95	A	39a
				13	E	39a
		*p*-MeC_6H_4	168–169	63	A	*m*
		*p*-MeC_6H_4	166–168	41	H	65b
Ph	Ph	*p*-MeC_6H_4	113	70	A	*i*
			111–112	94	A	10b
			106–107	83	D	28
			111–112	100	H	*n*
Ph	*o*-MeC_6H_4	*p*-MeC_6H_4	122–122.5	48	A	*o*
Ph	*o*-$MeOC_6H_4$	*p*-MeC_6H_4	161.5–162	62	A	*o*
p-$MeOC_6H_4$	*p*-$MeOC_6H_4$	*p*-MeC_6H_4	133–134		H	58
p-$H_2NC_6H_4$	*p*-$H_2NC_6H_4$	*p*-MeC_6H_4	230		A	*p*
$PhCH_2$	$PhCH_2$	*p*-MeC_6H_4	190–191	74	H	56
$PhCH_2$	CH_2CH_2Cl	*p*-MeC_6H_4	133–134		A	*j*
Me	*p*-$PC_6H_4CH_2$[q]	*p*-MeC_6H_4			A	*r*
Et	*p*-$PC_6H_4CH_2$[q]	*p*-MeC_6H_4			A	*r*
Ph	*p*-$PC_6H_4CH_2$[q]	*p*-MeC_6H_4			A	*r*

TABLE I (Continued)

R^1	R^2	R^3	Mp, °C	Yield, %	Method[a]	Ref
Me	Me	p-$MeOC_6H_4$	138.5–139.5	66	C	25
			139	48	F	42b
Me	Me	p-ClC_6H_4	117		A	*s*
Me	Ph	p-ClC_6H_4	98–98.5	65	A	112
n-C_6H_{13}	MeCH=CH	p-BrC_6H_4	74–82	62	A	*t*
n-Bu	n-Bu	p-BrC_6H_4	104–105		A	*t*
Me	Me	p-$O_2NC_6H_4$	187.5–188.5		A	*u*
			184–185	85	C	21
			186–187	90	C	25
$H_2C{=}CHCH_2$	$H_2C{=}CHCH_2$	p-$O_2NC_6H_4$	75–76.5		A	131a
Ph	Ph	p-$O_2NC_6H_4$	160–161		A	*u*
p-$MeCONHC_6H_4$	p-$MeCONHC_6H_4$	p-$MeCONHC_6H_4$	163		A	*p*
p-$H_2NC_6H_4$	p-$H_2NC_6H_4$	p-$H_2NC_6H_4$	245 dec		A	*p*
$PhCH_2$	$PhCH_2$	p-$PhN{=}NC_6H_4$	170–171 dec	55	A	*v*
Me	Me	F	50	94	E	*w*

[a] Method of preparation as described in section II. [b] H. C. Buchholt and A. Senning, *Acta Chem. Scand.*, **24**, 2255 (1970). [c] E. Behrend and A. Haas, *J. Fluorine Chem.*, **4**, 83 (1974). [d] A. Chrzaszczewska and W. Szalecki, *Lodz. Tow. Nauk, Wyd. 3, Acta Chim.*, **12**, 129 (1967); *Chem. Abstr.*, **71**, 124094 (1969). [e] D. Swern, I. Ikeda, and G. F. Whitfield, *Tetrahedron Lett.*, 2635 (1972). [f] F. G. Mann, *J. Chem. Soc.*, 958 (1932). [g] D. Leaver and F. Challenger, *J. Chem. Soc.*, 39 (1957). [h] M. Večeřa and J. Petránek, *Collect. Czech. Chem. Commun.*, **21**, 912 (1956). [i] Á. Kucsman, I. Kapovits, and M. Balla, *Tetrahedron*, **18**, 75 (1962). [j] T. P. Dawson, *J. Am. Chem. Soc.*, **69**, 968 (1947). [k] J. S. H. Davies and A. E. Oxford, *J. Chem. Soc.*, 224 (1931). [l] R. B. Greenwald, D. H. Evans, and J. R. DeMember, *Tetrahedron Lett.*, 3885 (1975). [m] D. Hellwinkel and G. Fahrback, *Justus Liebigs Ann. Chem.*, **715**, 68 (1968). [n] N. Furukawa, T. Yoshimura, T. Omata, and S. Oae, *Chem. Ind. (London)*, 702 (1974). [o] M. Moriyama, S. Oae, T. Numata, and N. Furukawa, *ibid.*, 163 (1976). [p] K. K. Andersen, J. Bhattacharyya, and S. K. Mukhopadhyay, *J. Med. Chem.*, **13**, 759 (1970). [q] P is polystyrene polymer support. [r] H. Kise, H. Serita, M. Seno, and T. Asahara, *Chem. Lett.*, 283 (1974). [s] C. Dell'Erba, G. Guanti, G. Leandri, and G. Poluzzi Corallo, *Int. J. Sulfur Chem.*, **8**, 261 (1973). [t] D. S. Tarbell and W. E. Lovett, *J. Am. Chem. Soc.*, **78**, 2259 (1956). [u] J. Petránek, M. Večeřa, and M. Jureček, *Collect. Czech. Chem. Commun.*, **24**, 3637 (1959). [v] R. Madeja, *Lodz. Tow. Nauk, Wyd. 3*, 53 (1955); *Chem. Abstr.*, **52**, 3710i (1958). [w] H. W. Roesky and A. Hoff, *Chem. Ber.*, **101**, 162 (1968).

Other *N*-halo compounds derived from amides, amidines, guanidines, ureas, and urethanes have also been found to react with sulfides to give sulfilimines in the presence of a base (Tables III and VIII). *N*-Chloro compounds are most frequently used; these may also be generated in situ by treating the amine or amide with *tert*-butyl hypochlorite. Anilines, amides, amidines, and heterocyclic amines have been converted into sulfilimines using the in situ technique (Tables III, V, VII, and VIII).

Salts of *N*-chloroarenesulfonamides have been found to give sulfilimines with sulfides of many types, including diaryl sulfides, but, with a few exceptions,[8,9] most other *N*-halo compounds have given sulfilimines only with dialkyl or alkyl aryl sulfides.

Two types of mechanism can be envisaged for these reactions: (a) nucleophilic attack by the sulfide on the *N*-halo compound (eq 1), with the formation of an azasulfonium salt, and (b) halogenation of the sulfide by the *N*-halo compound, followed by nucleophilic attack of the amine or amide, or its anion, on the halosulfonium salt (eq 2). The distinction between these mechanisms is less clearly defined if the involvement of a tetracovalent sulfurane intermediate, formed by oxidative addition of the *N*-halo compound to the sulfide, is considered (eq 3).

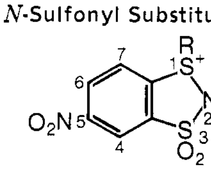
$$R^1R^2S + R^3NHX \longrightarrow R^1R^2\overset{+}{S}NHR^3\,\bar{X} \xrightarrow{\text{base}} R^1R^2\overset{+}{S}{-}\bar{N}R^3 \quad (1)$$

$$R^1R^2S + R^3NHX \longrightarrow R^1R^2\overset{+}{S}X\bar{N}HR^3 \xrightarrow{\text{base}} R^1R^2\overset{+}{S}{-}\bar{N}R^3 \quad (2)$$

$$R^1R^2S + R^3NHX \longrightarrow R^1R^2S\begin{smallmatrix}NHR^3\\X\end{smallmatrix} \xrightarrow{\text{base}} R^1R^2\overset{+}{S}{-}\bar{N}R^3 \quad (3)$$

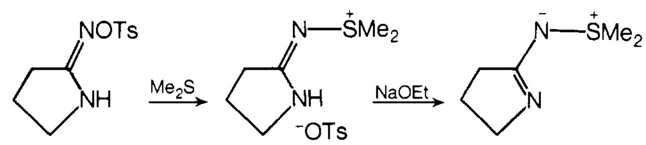
Kinetic investigations of reactions involving chloramine-T point to the mechanism of eq 2 as the more likely: a slow rate-determining chlorination of the sulfide is followed by rapid nucleophilic attack by the sulfonamide anion.[10] The second step may involve a sulfurane as an intermediate. Other nucleophiles can compete with the amide anion in the attack on the sulfonium salt; thus, water can give rise to the formation of sulfoxides, which are often formed as by-products in these reactions.[10,11] The relative yields of sulfilimines and sulfoxides depend upon the pH of the reaction medium,[10b] the solvent,[10a] and the groups on sulfur.[11] A reaction closely related to these is the reaction of the oxime tosylate **2** with dimethyl sulfide.[12]

TABLE II. Cyclic *N*-Sulfonyl Substituted Sulfilimines



R	Mp, °C	Yield, %	Method[a]	Ref
Me	238 dec	81	A	*b*
Et	156 dec	77	A	98
Bu	118 dec	58	A	98
C_6H_{13}	116 dec	63	A	98
C_8H_{17}	122 dec	92	A	98
Bu[t]	177–178	76	A	98
Ph	261–262	92	A	98
p-MeC_6H_4	213–214	80	A	98
p-ClC_6H_4	238 dec	92	A	*b*
$PhCH_2$	168–169	72	A	98
Et[c]	164	94	A	98

[a] Method of preparation as described in section II. [b] A. W. Wagner and R. Banholzer, *Chem. Ber.*, **96**, 1177 (1963). [c] The 5-NO_2 substituent is replaced by Me.



2 (92%)

B. Other Oxidative Addition Reactions of Sulfides

A second group of reagents which bring about the formation of sulfilimines from sulfides and amines or amides includes lead tetraacetate, *N*-chlorosuccinimide, and sulfuryl chloride. There is good evidence that initial oxidation occurs at sulfur with many

TABLE III. *N*-Acyl Substituted Sulfilimines, $R^1R^2S^+–\bar{N}COR^3$

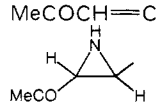
R^1	R^2	R^3	Mp (bp/mmHg), °C	Yield, %	Method[a]	Ref
Me	Me	Me	67–68	88	A	111
				78	A	100
Me	Me	CH_2Cl	92–94.5	70	B	*b*
Me	Me	$CHCl_2$	46–47		E	36
Me	Me	CCl_3	78–79		E	36
Me	Me	CF_3		60	E	37
Me	Me	MeO		60	F	45
Me	Me	EtO	Oil	73	F	52
				88	A	99, 107
					F	44
				62	E	40
Me	Me	Ph	108–109.5	47	C	24
				72	A	102
				35	F	43, 44
				34	F	51
				60	C	21
Me	Me	*p*-$MeOC_6H_4$	95–99	65	A	102
Me	Me	*p*-$O_2NC_6H_4$	217–218 dec	90	C	21
Me	Me	*p*-ClC_6H_4	92–93	60	E	40
Me	Me	*p*-BrC_6H_4	108–110	74	E	40
Me	Me	2-$C_{10}H_7CH_2$	93–94	28	C	24
Me	Me	NH_2	136–137	80	C	21
Me	Et	Me	59–60	94	A	111
Me	Ph	Me	Oil	91	A	55
Me	Ph	$CHCl_2$	99–100	10	A	101
Me	Ph	Ph	104.5–105	58	H	55
Me	Ph	NH_2	175–176	64	A	104
Me	*p*-MeC_6H_4	NH_2	168–169	55	A	104
Me	*p*-ClC_6H_4	NH_2	150–151	42	A	104
Me	*p*-$MeOC_6H_4$	NH_2	160–161	42	A	104
Et	Et	Me	(110–111/0.3)	81	A	100
				98	A	111
Et	Et	$CHCl_2$	112–113		C	20
Et	Et	$CHBr_2$	124–125	30	A	101
Et	Et	MeO		60	F	45
Et	Et	EtO	(135–140/0.05)	95	A	107
Et	EtSCH=CH	MeO			F	47
Et	Ph	NH_2	173–174	68	A	104
$–(CH_2)_4–$		Me	66–68	95	A	111
$–(CH_2)_4–$		$CHCl_2$	145–148	5	A	101
			149–151		C	20
$–(CH_2)_4–$		$CHBr_2$	154–157	11	C	101
$–(CH_2)_4–$		CCl_3	116–117		C	20
$–(CH_2)_4–$		Ph	116–117.5	35	C	24
n-Pr	*n*-Pr	Me	36–38	95	A	111
n-Pr	Ph	NH_2	122–123	50	A	104
n-Pr	*p*-MeC_6H_4	NH_2	119–120	59	A	104
i-Pr	*i*-Pr	Me	Oil	95	A	111
i-Pr	*i*-Pr	MeO		60	F	45
i-Pr	Ph	NH_2	122–123	67	A	104
n-Bu	Ph	NH_2	101–102	66	A	104
Ph	Ph	Me	86–87	95	H	55
			89	100	H	*c*
			177–179[d]	40	H	*e*
Ph	Ph	$CHCl_2$	73	10	A	101
Ph	Ph	*c*-C_3H_5	90.5–91	63	H	*f*
Ph	Ph	CHMePh	93–94	66	H	*f*
Ph	Ph	MeCOCH=CH		6	H	60
Ph	Ph			9	H	60
Ph	Ph	Ph	123–125	67	D	28
				60	H	*e*
				77	H	55
				100	H	*c*
Ph	Ph	*p*-MeC_6H_4	119–120	70	H	*f*
Ph	Ph	EtO	88–89	30	A	8
				44	H	55, *e*

TABLE III (Continued)

R^1	R^2	R^3	Mp (bp/mmHg), °C	Yield, %	Method[a]	Ref
			Oil	60	H	c
Ph	Ph	PhNH	133.5–135	83	H	55
				100	H	c
Ph	Ph	EtNH	87	95	H	54
Ph	Ph	$MeCH(OH)CH_2$	97–99	51	H	54
Ph	Ph	$MeCOCH_2$	67–68.5	75	H	54
Ph	Ph	o-$HO_2CC_6H_4$	157–157.5	95	H	54
Ph	Ph	$HO_2CCH_2CH_2$	130–131	88	H	54
Ph	p-$O_2NC_6H_4$	Me	104	95	H	54
$PhCH_2$	$PhCH_2$	Me	72–73		A	g
$PhCH_2$	$PhCH_2$	$CHCl_2$	120–121	8	A	101
$PhCH_2$	$PhCH_2$	Et	89		A	g
$PhCH_2$	$PhCH_2$	Ph	115		A	g

[a] Method of preparation as described in section II. [b] D. Swern, I. Ikeda, and G. F. Whitfield, *Tetrahedron Lett.*, 2635 (1972). [c] N. Furukawa, T. Yoshimura, T. Omata, and S. Oae, *Chem. Ind. (London)*, 702 (1974). [d] Mp of picrate. [e] Y. Tamura, K. Sumoto, J. Minamikawa, and M. Ikeda, *Tetrahedron Lett.*, 4137 (1972). [f] N. Furukawa, M. Fukumura, T. Nishio, and S. Oae, *J. Chem. Soc., Perkin Trans. 1*, 96 (1977). [g] M. V. Likhosherstov, *Zh. Obshch. Khim.*, **17**, 1478 (1947).

of these reagents; thus, dimethyl sulfide and tosyl amide gave the sulfilimine $Me_2S^+\bar{N}Ts$ with lead tetraacetate[13] in conditions where no reaction occurred between the oxidant and tosylamide.[14] Dimethyl sulfide forms a sulfonium salt with *N*-chlorosuccinimide which is stable below 0 °C and which reacts with aromatic amines to form azasulfonium salts,[15] from which sulfilimines can be generated using a base.[16,17] The course of the reaction can be changed by the presence of other nucleophiles; for example, the succinimidosulfonium salt reacts with primary and secondary alcohols to give alkoxysulfonium salts, from which aldehydes and ketones can be formed in excellent yields by the addition of triethylamine[18] (Scheme I).

The use of *N*-chlorosuccinimide has also been extended to other dialkyl sulfides, to alkyl aryl sulfides, and to bis(4-methoxyphenyl) sulfide;[16] sulfilimines have been prepared from anilines and heteroaromatic amines, amidines, and *N*-aminophthalimide (Tables V–VIII and XI). Other oxidants such as sulfuryl chloride[16] probably give sulfilimines by a similar mechanism. Lead tetraacetate is a less satisfactory reagent and gives good yields of sulfilimines in only a few systems, such as with *N*-aminophthalimide and other cyclic *N*-amino compounds where oxidation of the amine may be the initial reaction.[19]

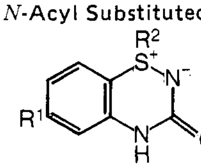
C. Reaction of Sulfoxides with Amines and a Dehydrating Agent

A third approach to the generation of activated sulfonium salts involves the attack on the oxygen atom of a sulfoxide by an electrophile. The resulting oxysulfonium salt **3** can then undergo nucleophilic attach by amines or amides to give azasulfonium salts, which can subsequently be converted to sulfilimines.

$$R^1R^2SO + X^+Y^- \rightarrow \underset{\mathbf{3}}{R^1R^2\overset{+}{S}{-}OX\;Y^-} \xrightarrow{R^3NH_2} R^1R^2\overset{+}{S}{-}NHR^3\;Y^- \rightarrow R^1R^2\overset{+}{S}{-}\bar{N}R^3$$

Activating agents which have been used in this sequence include acetic[20] and trifluoroacetic anhydrides,[21] phosphorus pentoxide,[20,22] phosphorus oxychloride,[23] dicyclohexylcarbodiimide,[24-26] methanesulfonyl chloride,[23] and aryl cyanates.[27] The reactions appear to work well only with dimethyl sulfoxide, although a few other sulfoxides have been used.[22] The relative merits of the various possible activating agents have been discussed by Swern and his co-workers, who conclude that trifluoroacetic anhydride is the most efficient and the most versatile.[21] Anilines, aryl amides, aryl sulfonamides, and urea can all be converted into the corresponding *S,S*-dimethylsulfilimines using

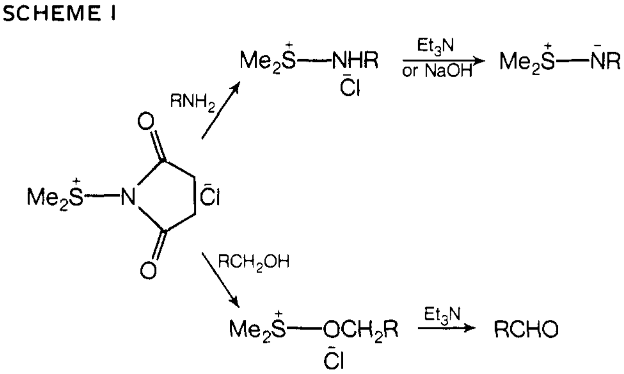
TABLE IV. Cyclic *N*-Acyl Substituted Sulfilimines



R^1	R^2	Mp, °C	Yield, %	Method[a]	Ref
H	Me	184	78	A	155
H	Ph	245	64	A	155
H	p-MeC_6H_4	217	66	A	155
H	$PhCH_2$	169	54	A	155
NO_2	Ph	251	52	A	155
NO_2	p-MeC_6H_4	248	47	A	155
Cl	$PhCH_2$	173	55	A	155

[a] Method of preparation as described in section II.

SCHEME I



dimethyl sulfoxide and trifluoroacetic anhydride (Tables I, III, and V). This reagent and those derived from sulfides and positive halogen compounds have generally superseded phosphorus pentoxide and other dehydrating agents.

D. Reaction of Diaryldialkoxysulfuranes with Amines and Amides

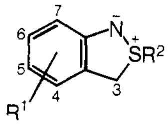
Although the methods so far described are fairly versatile with respect to the nature of the substituent on nitrogen, they are usually limited to sulfilimines with at least one alkyl group attached to sulfur. The most general method for preparing *S,S*-diarylsulfilimines has been developed by Martin and Franz,[28,29] who have made use of isolable diaryldialkoxysulfuranes such as diphenyldi(hexafluoro-2-phenyl-2-propoxy)sulfurane (**4**). The sulfuranes, which are prepared from diaryl sulfides, bromine, and potassium hexafluoro-2-phenyl-2-propoxide, react readily with ammonia, alkyl- and arylamines, primary amides, and sul-

TABLE V. *N*-Aryl Substituted Sulfilimines, $R^1R^2S^+\bar{N}Ar$

R^1	R^2	Ar	Mp, °C	Picrate mp, °C	Yield, %	Meth-od[a]	Ref
Me	Me	Ph	Oil	130–130.5 dec	60	C	21
					47	C	22
$-CH_2S(CH_2)_3-$		Ph	108–111		60	B	16
Ph	Ph	Ph	109.5–110.5		51	D	28
Me	Me	*o*-MeC_6H_4		165–166 dec	40	C	21
					95	C	22
$-CH_2S(CH_2)_3-$		*o*-MeC_6H_4	112–116	143–144	79	B	16
Me	Me	*p*-MeC_6H_4		165–166 dec	60	C	21
			40–45	165–167	70	C	22, 147
			52–55	163–167	69	B	16
Me	Me	*p*-$MeOC_6H_4$	44–45	117–121 dec	65	C	147
			45–47	117–121	88	B	16
Me	Me	*o*-FC_6H_4		140–141 dec	85	C	21
Me	Me	*o*-ClC_6H_4	58–60		60	C	*b*
			58–60		80	C	22
Me	Me	*m*-ClC_6H_4	50–52		83	C	22
					67	C	*b*
Me	Me	*p*-ClC_6H_4	64–66		52	C	*b*
			66–67	160–162	80	C	147
				160–162	92	B	16
Me	*n*-Pr	*p*-ClC_6H_4	Oil	124–128	90	B	16
Me	*i*-Pr	*p*-ClC_6H_4	Oil	140–142	76	B	16
Me	Ph	*p*-ClC_6H_4	77–79	133–135	55	B	16
Me	*p*-MeC_6H_4	*p*-ClC_6H_4	103–105	140–141	82	B	16
Me	$PhCH_2$	*p*-ClC_6H_4	96–100	148–149	88	B	16
Et	Et	*p*-ClC_6H_4	Oil		41	C	22
$-(CH_2)_4-$		*p*-ClC_6H_4	88–95		20	C	22
p-$MeOC_6H_4$	*p*-$MeOC_6H_4$	*p*-ClC_6H_4	Oil	133–134	74	B	16
$-CH_2S(CH_2)_3-$		*p*-ClC_6H_4	123–128	132–134	91	B	16
$-(CH_2)_2CHMe(CH_2)_2-$[c]		*p*-ClC_6H_4	149–153		80	B	148
$-(CH_2)_2CHMe(CH_2)_2-$[d]		*p*-ClC_6H_4	77–79		11	C	148
cis-$CHMeCH_2CHMeSCH_2-$[c]		*p*-ClC_6H_4	103–109		64	B	148
cis-$CHMeCH_2CHMeSCH_2-$[d]		*p*-ClC_6H_4	99–102		6	B	148
Me	Me	*p*-BrC_6H_4	72–74		45	C	22
Me	Me	*p*-NCC_6H_4	108–109		65	C	21
			110–112	184–185	57	B	16
				184–185	41	C	147
Me	*n*-Pr	*p*-NCC_6H_4	Oil	133–137	65	B	16
Me	Me	*p*-$MeO_2CC_6H_4$	80–82	178–182	83	B	16
				177–179	55	C	147
Me	*p*-MeC_6H_4	*p*-$RO_2CC_6H_4$[e]	Oil	108–110	52	B	16
Me	Me	*o*-$O_2NC_6H_4$	73–74		60	C	21
Me	Me	*m*-$O_2NC_6H_4$	100–101		85	C	26
			96–98		37	C	22
Me	Me	*p*-$O_2NC_6H_4$	148–151		35	C	22
			163–165		82	C	26
			167–168		70	E	40
			166–167 dec		65	C	21
Me	Me	*p*-$Me_2S^+\bar{N}SO_2C_6H_4$	179–182 dec		59	C	21
Me	Me	*p*-$H_2NSO_2C_6H_4$	135–137 dec		50	C	21
Me	Me	*p*-$RNHSO_2C_6H_4$[f]	265–268 dec		70	C	21
Me	Me	2-Me-4-ClC_6H_3	50–52		67	C	22, *b*
Me	Me	2-Me-4-BrC_6H_3	47–49		82	C	22, *b*
Me	Me	2-Cl-5-$O_2NC_6H_3$	127–128		71	B	129
Me	Me	2,4-$(O_2N)_2C_6H_3$	175–176		96	C	68
			181–182		34	H	56
$-(CH_2)_5-$		2,4-$(O_2N)_2C_6H_3$	138.5–139.5		92	H	56
Ph	Ph	2,4-$(O_2N)_2C_6H_3$	133.5–134		89	H	55, *g*
$PhCH_2$	$PhCH_2$	2,4-$(O_2N)_2C_6H_3$	125–126		52	H	56
Me	Me	3,5-$(O_2N)_2C_6H_3$	168–170		74	C	26
Me	Me	1-$C_{10}H_7$	76–79		72	C	22
Me	Me	2,4,6-$Me_3C_6H_2$	30–35		81	C	22
Me	Me	2,4,6-$Br_3C_6H_2$	78–80		27	C	22
Me	Me	2-Me-4-Cl-6-$MeSCH_2C_6H_2$	Oil		72	C	22

[a] Method of preparation as described in section II. [b] P. Claus and W. Vycudilik, *Tetrahedron Lett.*, 3607 (1968). [c] N-Aryl substituent is equatorial. [d] N-Aryl substituent is axial. [e] R = L-menthyl. [f] R = 2-pyrimidyl. [g] Y. Tamura, K. Sumoto, J. Minamikawa, and M. Ikeda, *Tetrahedron Lett.*, 4137 (1972).

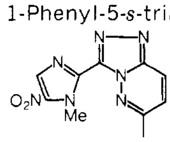
TABLE VI. Cyclic *N*-Aryl Substituted Sulfilimines



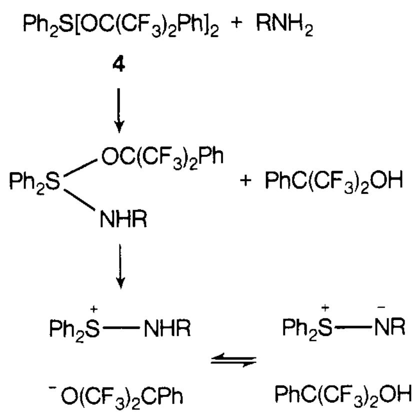
R^1	R^2	Mp, °C	Picrate mp, °C	Yield, %	Method[a]	Ref
H	Me	Oil	160–162	70	B	116
5-Me	Me	Oil	150–152	80	B	116
5-Cl	Me	101–109	172–173	95	B	116
5-Cl	*p*-MeC_6H_4	Oil	132–134	37	B	116
7-Cl	Me	89–92	170–173	95	B	116
5-CN	Me	136–138	180–183	73	B	116
5-NO_2	Me	142–145	180–183	76	B	116
5-CO_2Me	Me	113–117	188–191	76	B	116

[a] Method of preparation as described in section II.

TABLE VII. *N*-Heteroaryl Substituted Sulfilimines, $R^1R^2S^+–\bar{N}R^3$

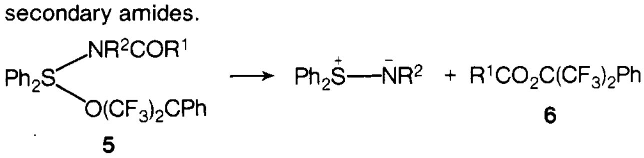
R^1	R^2	R^3	Mp, °C	Picrate mp, °C	Yield, %	Method[a]	Ref
Me	Me	2-Pyridyl	86–88		63	B	16
			Oil	127–130	87	B	117
$–CH_2S(CH_2)_3–$		2-Pyridyl	132–135	117–119	56	B	16
Me	Me	3-Methyl-2-pyridyl	Oil	185 dec	76	B	117
Me	Me	6-Methyl-2-pyridyl	Oil	136	85	B	117
Me	Me	2-Pyrazinyl	Oil	148–150	54	B	117
Me	Me	2-Pyrimidyl			33	A	117
Me	Me	4-Methyl-2-pyrimidyl				A	117
Me	Me	4,6-Dimethyl-2-pyrimidyl				A	117
Me	Me	2-Benzoxazolyl	139–141		67	A	127
Me	Me	1-Phenyl-5-*s*-triazolyl	91–93		28	A	*b*
Me	Me					C	187b

[a] Method of preparation as described in section II. [b] T. L. Gilchrist, C. J. Moody, and C. W. Rees, unpublished result.



fonamides, to give diarylsulfilimines in good yields.[28] The reaction probably involves an intermediate amido- or aminosulfurane, as shown. The more basic sulfilimines (derived from ammonia and alkylamines) are formed as alcoholates by this procedure, but the hexafluoro-2-phenyl-2-propanol can be removed by extraction with aqueous alkali.

The sulfurane **4** also reacts with secondary amides to give *S,S*-diphenylsulfilimines.[29] The intermediate amidosulfuranes **5** collapse to the sulfilimines and esters **6**, except in cases where R^2 is a bulky group. The reaction is a useful method of cleaving secondary amides.



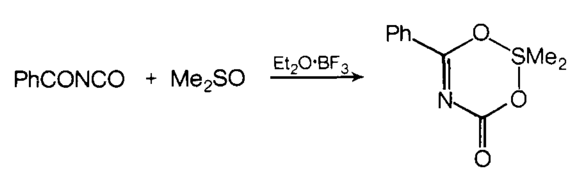
E. Reaction of Sulfoxides with Isocyanates, Sulfinylamines, and Related Compounds

Dimethyl sulfoxide and other dialkyl sulfoxides react exothermically with arenesulfonyl isocyanates and give sulfilimines in good yields.[30,31] Similar reactions take place between sulfoxides and sulfinylamines[31–35] or sulfur diimides[32,34,35] (eq 4). Both alkyl and aryl sulfoxides react with *N*-sulfinyltosylamide, but the latter require heating.[33]

$$R^1R^2SO + R^3SO_2N{=}X{=}Y \rightarrow R^1R^2\overset{+}{S}{-}\overset{-}{N}SO_2R^3 + O{=}X{=}Y \quad (4)$$

$$XY = CO,\ SO,\ S{=}NSO_2R^3$$

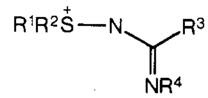
Dimethyl sulfoxide has also been found to react with several acyl isocyanates RCONCO (R = $CHCl_2$, CCl_3, CF_3, and Ph).[36,37] Acylsulfilimines were obtained from the haloacyl isocyanates, but benzoyl isocyanate reacted differently: in the presence of a catalytic amount of boron trifluoride etherate a crystalline 1:1 adduct, which was formulated as the sulfurane **7**, was isolated.[37]



7 (80%)

The reactions of sulfoxides with tosyl isocyanate, *N*-sulfinyltosylamide, and *N,N'*-bis(tosyl)sulfur diimide have been the subject of detailed mechanistic investigation, notably by Cram

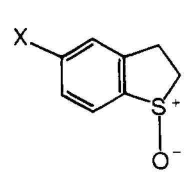
TABLE VIII. *N*-Imidoyl Substituted Sulfilimines



R^1	R^2	R^3	R^4	Mp, °C	Yield, %	Method[a]	Ref
Me	Me	Me	Ph	Gum 187–189[b]	84	A	17
Me	Me		$-(CH_2)_3-$	Oil 137[b]		A	12
Me	Me	Ph	H	67–68	80	A	152
Me	Me	Ph	Ph	167–169	60	A	17
Me	Me	Ph	o-MeC_6H_4	170–172	67	A	17
Me	Me	Ph	o-ClC_6H_4	172–174	65	A	17
Me	Me	Ph	p-ClC_6H_4	180–182	62	A	17
Me	Me	Ph	2,6-$Me_2C_6H_3$	211–213	41	B	154
Me	Me	Ph	2,6-$Cl_2C_6H_3$	204–206	71	B	*c*
Me	Me	Ph	2,6-$Et_2C_6H_3$	175–180	41	B	154
Me	Me	Ph	2,4,6-$Me_3C_6H_2$	184–186	38	B	154
Me	Me	Ph	$PhCH_2$	105–106	63	A	17
Me	Me	Ph	2-Pyridyl	170–172	35	A	17
Me	Me	Ph	COMe	114–116	60	*d*	152
Me	Me	Ph	COPh	188–190	66	*d*	152
Me	Me	Ph	CO-p-MeC_6H_4	172–173	54	*d*	152
Me	Me	Ph	NMe_2	120–121	92	A	*c*
$-(CH_2)_4-$		Ph	Ph	131–133	65	B	17
Ph	Ph	Ph	Ph	141–143	50	H	17
Ph	Ph	Ph	o-MeC_6H_4	138	40	H	17
Ph	Ph	Ph	o-ClC_6H_4	165–167	22	H	17
Ph	Ph	Ph	p-$O_2NC_6H_4$	135–137	92	H	*c*
Ph	Ph	Ph	2,6-$Me_2C_6H_3$	127–129	62	H	*c*
Ph	Ph	Ph	2,3,5,6-Me_4-4-O_2NC_6	192–194	76	H	*c*
Ph	Ph	Ph	2-Benzothiazolyl	163.5–165	78	H	*c*
Ph	Ph	H	NH_2	72	58	A	9
$PhCH_2$	$PhCH_2$	Ph	Ph	122–124	67	A	17

[a] Method of preparation as described in section II. [b] Mp of picrate. [c] T. L. Gilchrist, C. J. Moody, and C. W. Rees, unpublished results. [d] Prepared from the sulfilimine where R^4 = H by acylation.

and his co-workers. The conversion of chiral sulfoxides into *N*-tosylsulfilimines has been studied as a part of a reaction cycle which allows the stereochemistry of various substitution reactions at sulfur to be investigated.[35] Thus, the sulfoxide **8** of known absolute stereochemistry was converted into the sulfilimine **9**, the absolute stereochemistry of which was determined using melting point composition diagrams. With *N*-sulfinyltosylsulfonamide and with *N,N*-bis(tosyl)sulfur diimide in dry pyridine at 0 °C the reactions were highly stereoselective and termolecular, and went with inversion of configuration at sulfur.[35] In benzene, however, the reaction of the sulfoxide with *N,N*-bis(tosyl)sulfur diimide went with retention of configuration at sulfur and was a bimolecular process.[35,38a] Similar results were obtained with the cyclic sulfoxides **10** but the reactions were faster.[32] With

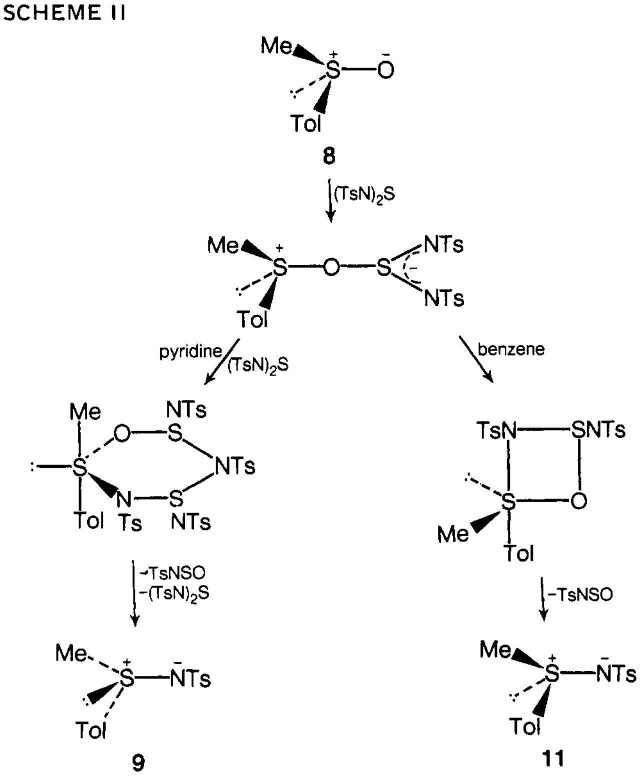


10, X = H, Br

tosyl isocyanate in acetonitrile at 25 °C the sulfoxide **8** gave the sulfilimine **9**, again with net inversion of configuration, but both the starting material and the product were competitively racemized in these conditions.[31]

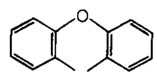
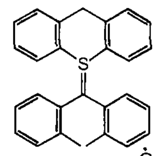
The first step in these reactions, which is illustrated in Scheme II for the reaction between (+)-(*R*)-methyl *p*-tolyl sulfoxide (**8**) and *N,N*[1]-bis(tosyl)sulfur diimide, is assumed to be nucleophilic attack by the oxygen of the sulfoxide to give a zwitterionic intermediate. In a nucleophilic solvent such as pyridine this is stabilized sufficiently to allow the attack of a second mole of the

SCHEME II



reagent, giving a six-membered ring sulfurane intermediate. If, as shown in Scheme II, both incoming and leaving groups occupy equatorial positions, the decomposition of the sulfurane will give

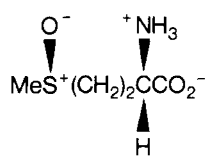
TABLE IX. *N*-Unsubstituted Sulfilimines, $R^1R^2S^+{-}\bar{N}H$

R^1	R^2	Mp (bp/mmHg), °C	Picrate mp, °C	Yield, %	Method[a]	Ref
Me	Me	(39/0.4)		85	G	63
			104		G	115
Me	Ph	Oil	112–112.5		G	114
Me	p-MeC_6H_4	20		70	G	74
			158–159	95	G	54
Et	Et	−11.8 to −12		98	G	63
			110–111		G	114, 115
Et	Ph	Oil	90–91		G	114
c-C_3H_5	p-MeC_6H_4		138–139	95	G	54
$-(CH_2)_5-$		Oil	191	100	G	114
Ph	Ph	58–60		48	D	28
		71[b]		75	G	114
				90	G	55
Ph	p-MeC_6H_4	54–54.5		100	G	114
Ph	o-MeC_6H_4	83.5–84.5		97	G	54
Ph	p-ClC_6H_4	Oil		100	G	114
		48–49		77	G	54
Ph	m-ClC_6H_4	35–36			G	54
Ph	p-$O_2NC_6H_4$	95.5–97.5		76	G	114
		93–95		95	G	56
		98–99		95	G	54
Ph	o-$O_2NC_6H_4$	104–104.5		79	G	54
p-$MeOC_6H_4$	p-$MeOC_6H_4$	57–58	123	93	G	58
		55–7		78	G	56
		66–67 dec		88	I	65b
		165–166		81	G	56
CF_3	CF_3			55	G	c

[a] Method of preparation as described in section II. [b] Monohydrate. [c] S. D. Morse and J. M. Shreeve, *J. Chem. Soc., Chem. Commun.*, 560 (1976).

a sulfimide of inverted configuration. In a nonnucleophilic solvent such as benzene, the zwitterion may collapse to a four-membered ring sulfurane, in which the incoming group is axial and the outgoing group is equatorial; subsequent decomposition of this sulfurane will give a sulfimide of retained configuration, **11.** These reactions form part of a much more general picture of substitution reactions at sulfur, in which other types of molecule can combine with zwitterionic intermediates to form cyclic sulfuranes.[31,32] Apart from the unattractive feature that the more electronegative groups in the six-membered ring sulfurane occupy equatorial positions, this scheme accounts well for the kinetics and stereochemistry of the reactions.

Similar reactions have been reported with 4-*tert*-butylthiane 1-oxides,[39] but methionine sulfoxide (**12**) was reacted, via its



12

N-phthaloyl derivative, with *N*-sulfinyltosylamide in pyridine to give a sulfilimine of retained configuration.[38b] The unusual stereochemical course of this reaction may be determined by participation of the neighboring carboxyl group in the reaction.[38a]

There are a few examples of related reactions which have been used to prepare sulfilimines. Dimethyl sulfoxide reacts with several imidosulfurous dichlorides in ether at room temperature to give sulfilimines with the elimination of thionyl chloride (eq 5). The reaction appears to be more general, with respect to the nitrogen substituent, than others of this type, and examples are reported with arenesulfonyl, acyl, ethoxycarbonyl, and aryl groups.[40]

$$Me_2SO + Cl_2SNR \rightarrow Me_2\overset{+}{S}{-}\bar{N}R + SOCl_2 \quad (5)$$

An interesting extension of the reaction with isocyanates is the observation that one sulfilimine can be converted into another: *S,S*-diphenyl-*N*-methylsulfilimine was found to react exothermically with phenyl isocyanate, giving triphenylsulfilimine in low yield.[28]

$$Ph_2S{-}\bar{N}Me + PhNCO \rightarrow Ph_2\overset{+}{S}{-}\bar{N}Ph \quad (10\%)$$

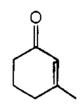
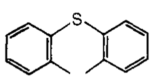
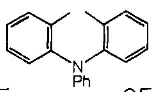
Sulfilimines are also formed in the reaction of dialkyl sulfides with di-*N*-tosylsulfur diimide.[41]

$$R_2S + TsN{=}S{=}NTs \rightarrow R_2\overset{+}{S}{-}\bar{N}Ts \quad (35\text{–}80\%)$$

F. Routes Involving Azides and Related Compounds

The photolysis of several organic azides in the presence of an excess of a dialkyl sulfide leads to the formation of sulfilimines. Reactions of this type have been observed with arenesulfonyl,[42] acyl,[43,44] and alkoxycarbonyl azides.[44,45] It is likely that the reactions involve singlet nitrenes as intermediates; these electrophilic species are then intercepted by the sulfide.

TABLE X. *N*-Alkyl Substituted Sulfilimines, $R^1R^2S^+{-}\bar{N}R^3$

R^1	R^2	R^3	Mp, °C	Yield, %	Method[a]	Ref
Me	Ph	$(NC)_2C{=}CH$	149–150	96	H	55
Me	Ph	$(NC)(EtO_2C)C{=}CH$	117–118	71	H	55
Ph	Ph	Me	79–80	85	D	28
Ph	Ph	*i*-Pr	34–35.5	98	D	28
Ph	Ph	*n*-Bu	Oil	98	D	28
Ph	Ph	*t*-Bu	47–49	82	D	28
Ph	Ph	n-C_6H_{13}	Oil	51	H	59
Ph	Ph	$PhCH_2$	65.5–66.5	93	D	28
			62–64	77	H	59
Ph	Ph	$NCCH_2CH_2$	Oil	69	H	60
Ph	Ph	$PhCH_2CH_2$	Oil	54	H	59
Ph	Ph	PhMeCH	Oil	71	H	59
Ph	Ph	1-$C_{10}H_7CH_2$	Oil	74	H	59
Ph	Ph	$PhSO_2CH_2CH_2$	Oil	100	H	60
Ph	Ph	EtO_2CMeCH	Oil	54	H	59
Ph	Ph	EtO_2CEtCH	Oil	38	H	59
Ph	Ph	PhCOCH=C(COPh)	131–133	90	H	55
Ph	Ph	PhCOCH=CPh	119–122	68	H	55
Ph	Ph	PhCOCH=CH	Oil	68	H	55
Ph	Ph	$(NC)_2C{=}CH$	129–131	40	H	55
Ph	Ph	$(NC)(EtO_2C)C{=}CH$	167–172	71	H	55
Ph	Ph	$(NC)_2C{=}C(CN)$	139–140	87	H	55
Ph	Ph		152–153	82	H	61
Ph	m-$O_2NC_6H_4$	Me	81.3–82.5	65	D	28
		*t*-Bu	148–149		I	*b*
		$PhCH_2$	142–143	88	I	65a
CF_3	CF_3	$(CF_3)_2CF$	(89.1)	71	*c*	*d*
CF_3	CF_3	$(CF_3)_2C{=}N(CF_3)_2C$	(136.6)	82	*c*	*d*

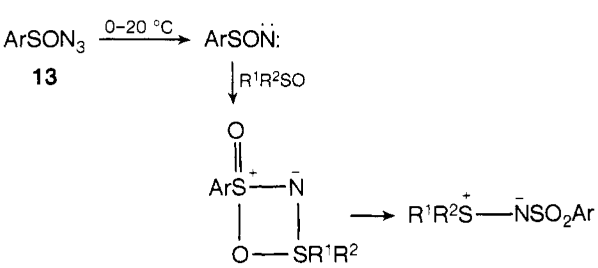
[a] Method of preparation as described in section II. [b] H. J. Shine and K. Kim, *Tetrahedron Lett.*, 99 (1974). [c] Prepared from $(CF_3)_2SF_2$ and $LiN{=}C(CF_3)_2$. [d] R. F. Swindell and J. M. Shreeve, *J. Am. Chem. Soc.*, **94**, 5713 (1972).

$$R^3CON_3 \xrightarrow{h\nu} R^3CO\ddot{N}\!: \xrightarrow{R^1R^2S} R^1R^2\overset{+}{S}{-}\overset{-}{N}COR^3$$

Evidence to support the intermediacy of singlet nitrenes was obtained by investigating the effect of triplet sensitizers on the reactions. The formation of sulfilimines was inhibited by the presence of the sensitizers, showing that triplet nitrenes did not react in this way.[45]

Attempts to form sulfilimines by the thermal decomposition of azides in the presence of sulfides have not been very successful, because the sulfilimines are unstable at the temperatures required to decompose the azides. Reactions of this type in which decomposition products of the sulfilimines have been detected have been reported with alkoxycarbonyl azides[46,47] and with hydrazoic acid;[48] a sulfilimine was isolated in one case.[47] Cyanogen azide is exceptional in that it has a low decomposition temperature; it is claimed that *N*-cyanosulfilimines can be formed in good yield from cyanogen azide and sulfides at 20–60 °C.[49]

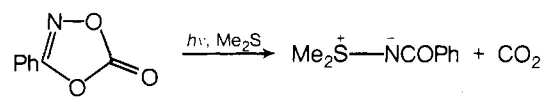
An unusual reaction occurs with arenesulfinyl azides **13** in



13

acetonitrile containing dimethyl sulfoxide at 0–20 °C; the products, which are isolated in good yield, are arenesulfonyl sulfilimines.[50] It is suggested that these reactions involve four-center addition of the sulfinyl nitrene to dimethyl sulfoxide. Evidence in support of this proposal comes from a kinetic investigation, which shows that the rate of decomposition of the azides is independent of the concentration of the sulfoxide, and from an experiment using an optically active sulfoxide, which shows that the configuration of the sulfoxide is retained in the sulfilimine.

Sulfilimines have also been isolated from reactions of sulfides with a few other nitrene precursors. Photolysis of 5-phenyl-1,3,4-dioxazol-2-one (**14**) in dimethyl sulfide gave *N*-benzoyl-*S*,*S*-dimethylsulfilimine (34%).[51]



14

Treatment of 4-nitrophenylsulfonyloxyamines **15** with triethylamine in the presence of dimethyl sulfide also gave the corresponding sulfilimines (36–78%).[52]

$$\underset{\mathbf{15}}{RNHOSO_2C_6H_4\text{-}4\text{-}NO_2} \xrightarrow{Et_3N,\,Me_2S} Me_2\overset{+}{S}{-}\overset{-}{N}R$$

$R = ArSO_2, EtOCO$

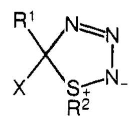
There is good evidence that oxidation of *N*-aminophthalimide (**16**) by lead tetraacetate involves singlet phthalimidonitrene as

TABLE XI. Other Sulfilimines, $R^1R^2S^+\text{—}\bar{N}X$

R^1	R^2	X	Mp, °C	Yield, %	Method[a]	Ref
Me	Me	CN	81.8–83	98	F	49,*b*
Me	c-C_6H_{11}	CN	78.5–79.5	95	F	49
Me	*p*-ClC_6H_4	CN	107–108	90	F	49
$Me(CH_2)_{11}$	$Me(CH_2)_{11}$	CN	49.5–63	99	F	49
Ph	Ph	CN	62–63	65	B	*b*
Ph	Ph	Cl	116–117 dec	100	H	62
Ph	Ph	Br	96–97 dec	100	H	62
Ph	Ph	I	99–100 dec	100	H	62
Me	Me	Phthalimido	133–134 dec	90	B	118
Ph	Ph	PhNHCS	138.5	95	H	54

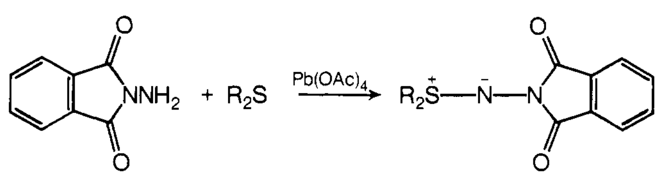
[a] Method of preparation as described in section II. [b] D. Swern, I. Ikeda, and G. F. Whitfield, *Tetrahedron Lett.*, 2635 (1972).

TABLE XII. 1,5-Dihydro-1,2,3,4-thia(S^{IV})triazoles



R^1	R^2	X	Mp, °C	Yield, %	Method	Ref
Me	Me	NMe_2	83 dec	61	*a*	153
Ph	Me	NMe_2	80 dec	58	*a*	153
Ph	Me	Morpholino	103 dec	93	*a*	153
Ph	Et	Morpholino	80 dec	89	*a*	153
Ph	Allyl	Morpholino	93 dec	69	*a*	153
$PhCH_2$	Me	Morpholino	100 dec	92	*a*	153

[a] Prepared from $R^1C(X){=}S^+R^2\ I^-$ and NaN_3.



16 (70–90%) R = Me, Et

an intermediate.[53] Oxidation in the presence of dimethyl or diethyl sulfide gave the corresponding sulfilimines in good yield, and with other sulfides, products arising from unstable sulfilimines were isolated.[19]

Sulfilimines can themselves act as sources of nitrenes in photochemical reactions, and the irradiation of *S,S*-dimethyl-*N*-ethoxycarbonylsulfilimine in the presence of diethyl sulfide results in the formation of the *S,S*-diethylsulfilimine.[44]

G. Preparation of N-Unsubstituted Sulfilimines

N-Unsubstituted *S,S*-diarylsulfilimines are reasonably stable compounds for which special synthetic routes are available. They are useful intermediates in the preparation of several other types of *S,S*-diarylsulfilimines (section II.H). N-Unsubstituted sulfilimines derived from dialkyl or alkyl aryl sulfides are unstable at ambient temperatures but can be isolated as picrates.[54]

N–H sulfilimines can be prepared by direct amination of sulfides. The best reagent is *O*-mesitylenesulfonyl hydroxylamine,[55,56] but hydroxylamine-*O*-sulfonic acid[57,58] and chloramine[57] have also been used.

$$R^1R^2S + NH_2X \rightarrow R^1R^2\overset{+}{S}NH_2\ \bar{X} \xrightarrow{\text{base}} R^1R^2\overset{+}{S}\text{—}\bar{N}H$$

$$X = OSO_2Mes,\ OSO_2H,\ Cl$$

N–H sulfilimines are also readily available from the reaction of *N*-tosylsulfilimines with concentrated sulfuric acid at room temperature; yields of diarylsulfilimines are excellent.[54]

$$R^1R^2\overset{+}{S}\text{—}\bar{N}\,Ts \xrightarrow{H_2SO_4} R^1R^2\overset{+}{S}NH_2\ \overline{O}Ts \xrightarrow{NaOH} R^1R^2\overset{+}{S}\text{—}\bar{N}H$$

In both of the above procedures, diphenylsulfilimine is isolated as a hydrate. Anhydrous *S,S*-diphenylsulfilimine can be prepared by the method of Franz and Martin[28] (section II.D).

A less efficient method for preparing *S,S*-diarylsulfilimines is the reaction of *S,S*-diarylsulfur dichlorides with ammonia.[58]

$$Ar_2SCl_2 + 3NH_3 \rightarrow Ar_2\overset{+}{S}\text{—}\bar{N}H + 2NH_4Cl$$
$$(45\%)$$

H. Substitution of N–H Sulfilimines

Electrophilic substitution of N-unsubstituted *S,S*-diarylsulfilimines is an important route to several types of sulfilimines. Examples of such reactions involving the introduction of carbon substituents are shown in Scheme III, and those involving the introduction of heteroatom substituents are shown in Scheme IV.

Reactions of a similar type which have been reported for *S,S*-dialkylsulfilimines include that with carbon dioxide, giving the betaines **17** (R = Me or Et)[63] (eq 6) and an attempted nitrosation of diethylsulfilimine with nitrosyl chloride, which resulted in the formation of diethyl sulfide and nitrous oxide[64] (eq 7).

$$R_2\overset{+}{S}\text{—}\bar{N}H + CO_2 \xrightarrow{\text{ether}} R_2\overset{+}{S}\,NHCO_2^- \quad (6)$$

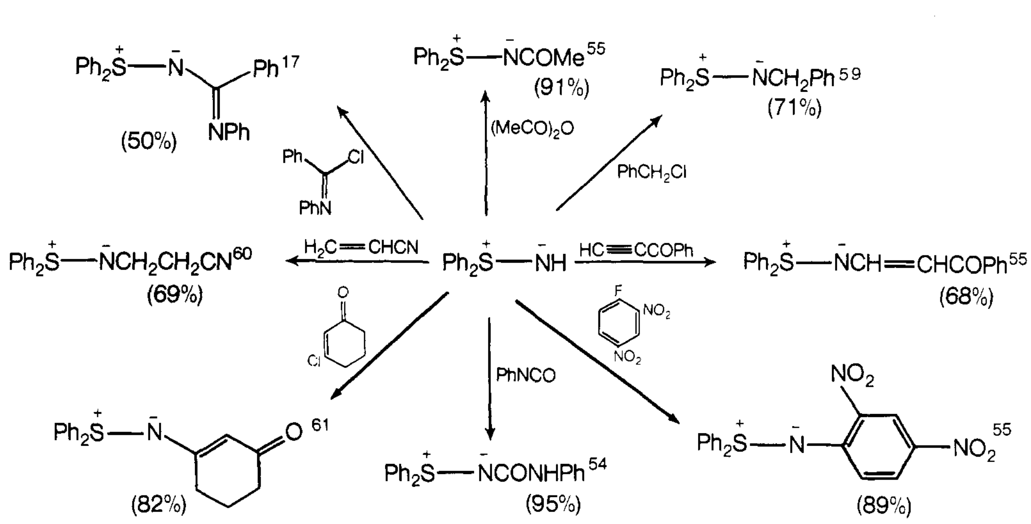
17

$$2Et_2\overset{+}{S}\text{—}\bar{N}H + NOCl \longrightarrow [Et_2\overset{+}{S}\text{—}\bar{N}NO] + Et_2\overset{+}{S}NH\ \bar{C}l \quad (7)$$
$$\downarrow$$
$$Et_2S + N_2O$$

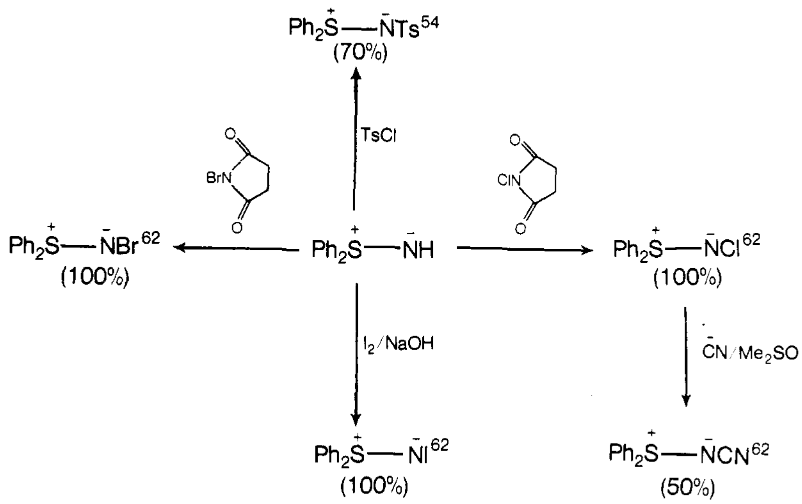
I. Miscellaneous Methods

Radical cation perchlorates of the general structure **18** react

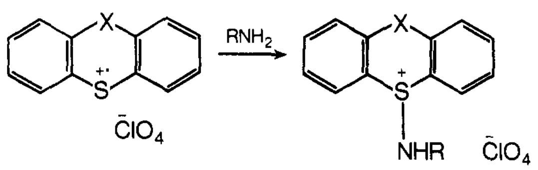
SCHEME III



SCHEME IV



with ammonia or primary alkylamines to give azasulfonium salts, from which sulfilimines can be liberated.[65]



18, X = S, O, NMe, NPh

Another approach to the synthesis of sulfilimines which has so far been explored very little is the nucleophilic displacement of halide from imidosulfurous dihalides. *N*-Phenylimidosulfurous difluoride is reported to react with phenyllithium to give triphenylsulfilimine[66] (eq 8), but an attempt to displace chloride from the ylide $ArS^{+}ClNSO_2Ph$ by the anion of tetraphenylcyclopentadiene was unsuccessful.[67]

$$F_2SNPh + 2PhLi \rightarrow Ph_2\overset{+}{S}\text{—}\overset{-}{N}Ph + 2LiF \quad (8)$$

A ligand exchange reaction takes place (eq 9) when *S*,*S*-dimethyl-*N*-2,4-dinitrophenylsulfilimine is heated with tosylamide in dimethylformamide.[68]

$$Me_2\overset{+}{S}\text{—}\overset{-}{N}Ar + TsNH_2 \xrightarrow{\text{DMF/90 °C}} \underset{(58\%)}{Me_2\overset{+}{S}\text{—}\overset{-}{N}Ts} + ArNH_2 \quad (9)$$

Ar = $2,4\text{-}(NO_2)_2C_6H_3$

III. Structure and Spectroscopic Properties

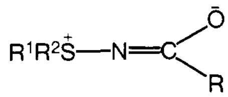
A. Structure and Bonding

Ylides derived from second-row elements have a greater range of possible bonding interactions open to them than their counterparts formed from elements in the first row of the periodic table. In particular there exists the possibility that electron density can be transferred from the anionic center to a vacant 3d orbital on the second-row element. A description of this type of interaction in sulfur ylides, and its expected consequences, has been given by Price and Oae.[69] If such bonding makes an important contribution to the structure of sulfilimines, they are more properly represented as resonance hybrids:

$$R^1R^2\overset{+}{S}\text{—}\overset{-}{N}R^3 \leftrightarrow R^1R^2S{=}NR^3$$

Much of the physical data on sulfilimines, including that from x-ray crystal structure determinations, have been interpreted as supporting the existence of such bonding in sulfilimines. Semiempirical molecular orbital calculations reported by Hoffmann and his co-workers on phosphonium ylides led them to conclude that $d\pi$–$p\pi$ interaction makes a significant contribution to the stabilization of such ylides.[70] Recently, however, it has been suggested that the ability of sulfur to stabilize an adjacent carbanion is due to the high polarizability of sulfur rather than to the participation of d orbitals in the bonding.[71] An x-ray crystal structure analysis of an azasulfonium betaine has shown that the nitrogen atom is sp^3 hybridized and not sp^2 hybridized as would be expected if $d\pi$–$p\pi$ conjugation were important.[72] The problem of the exact nature of the bonding in sulfilimines thus remains open at present.

The electron-accepting properties of the substituents on nitrogen are important in determining the stability of the sulfilimines. In the case of acylsulfilimines there is good evidence (particularly from x-ray and infrared data) that the negative charge is mainly concentrated on oxygen, so that these ylides are best represented by a zwitterionic structure.



Sulfilimines derived from unsymmetrically substituted sulfides can exist in optically active forms. This was first shown for *N*-tosylsulfilimines prepared from 3-(alkylthio)benzoic acids, which were resolved through their brucine salts;[73] other methods of preparing optically active sulfilimines include the use of chiral sulfoxides[37] and sulfonium salts[74,75] as precursors.

The optical activity of sulfilimines is undoubtedly due to the appreciable energy barrier to pyramidal inversion at sulfur. The barrier has been estimated as 24.4 kcal mol^{-1} in the model system $H_2S^+\bar{N}H$ on the basis of ab initio SCF molecular orbital calculations,[76] and enthalpies of activation for the racemization of a few sulfilimines have been determined experimentally.

S-Aryl-*S*-methyl-*N*-tosylsulfilimines racemize readily when heated in solution at 80–100 °C; the reaction is first order in sulfilimine and is relatively unaffected by the nature of the solvent. Activation enthalpies for the *S*-4-chlorophenyl[77] and *S*-4-tolyl[78] compounds are respectively 27.9 and 28.7 kcal mol^{-1}, these values being higher than for the corresponding sulfonium salts but lower than for the sulfoxides. For optically active *N*-acetyl-*S*-ethyl-*S*-methylsulfilimine the activation enthalpy is 34.1 kcal mol^{-1}, about 5 kcal mol^{-1} higher than for the corresponding sulfonium salt.[75] Attempts have been made to explain these differences in terms of the relative strengths of the 2p–3d bonds;[75,77,78] they have also been ascribed to the extent of repulsive interaction between lone pairs on sulfur and the adjacent heteroatoms in sulfoxides and sulfilimines.[75]

An x-ray crystal structure determination of *S,S*-dimethyl-*N*-methylsulfonylsulfilimine shows that it consists of a racemic mixture of two enantiomers.[79,80] The existence of enantiomers in such a sulfilimine derived from a symmetrical sulfide depends upon the configurational stability of the S(IV)–N bond, but this is not maintained in solution.[80,81] Partial rotation about the S(IV)–N bond occurs easily in solution; this precludes resolution of such compounds and is reflected in the NMR spectrum, which shows a single S(IV)–methyl signal.[82] The calculated barrier to rotation about the S(IV)–N bond in the model compound H_2S^+—$\bar{N}H$ is small (9.60 kcal mol^{-1}).[76]

The preferred conformations of sulfilimines derived from thianes have been determined by NMR. *N*-Arenesulfonylsulfilimines have a small preference for a conformation in which the imide group is axial,[83] but NH[83] and *N*-4-chlorophenyl[84] derivatives preferentially exist in a conformation with the imide group equatorial.

B. X-Ray Crystal Structure Determinations

X-Ray crystal structure analyses have been performed on several *N*-tosylsulfilimines, including the *S,S*-dimethyl,[85] *S,S*-diphenyl,[86] and *S*-methyl-*S*-phenyl[87] derivatives, and on *S,S*-dimethyl-*N*-methanesulfonylsulfilimine.[79,88] All these structures show very similar features, and the nature of the substituents in *N*-sulfonylsulfilimines has very little effect on the bonding. Both the SN bond lengths are shorter than might be expected for a sulfur–nitrogen single bond: that between the sulfonium sulfur and nitrogen lies in the range 1.628–1.636 Å, and that in the sulfonamide group is between 1.58 and 1.60 Å. The torsion angle of the SNSO system in these sulfilimines is in the range 31–37°; the distance between the sulfonium sulfur and the nearer of the oxygen atoms on the sulfonamide group is less than the sum of their van der Waals radii, indicating that some attractive interaction is possible.

TABLE XIII. Dipole Moments of Sulfilimines

Sulfilimine	μ, D	Ref
$Me_2S^+\bar{N}Ts$	7.02	91
$PhS^+Me\bar{N}Ts$	7.46	91
p-$NO_2C_6H_4S^+Me\bar{N}Ts$	6.73	91
p-$BrC_6H_4S^+Me\bar{N}Ts$	6.62	91
p-$ClC_6H_4S^+Me\bar{N}Ts$	6.57	91
p-$MeCOC_6H_4S^+Me\bar{N}Ts$	6.18	91
p-$MeCOC_6H_4S^+Me\bar{N}Ts$	7.75	91
p-$Me_2NC_6H_4S^+Me\bar{N}Ts$	8.87	91
$Me_2S^+\bar{N}C_6H_4$-o-Cl	1.56[a]	92
$Me_2S^+\bar{N}C_6H_4$-m-Cl	1.61[a]	92
$Me_2S^+\bar{N}C_6H_4$-p-Cl	1.81[a]	92

[a] These values have been questioned in later work; see Addendum and ref 227.

X-Ray analyses have also been reported for two acylsulfilimines. *N*-Dichloroacetyl-*S,S*-diethylsulfilimine contains a nearly planar SNCO system, with sulfur and oxygen atoms syn.[89] The bond lengths are: S–N, 1.673 Å; N–C, 1.344 Å; and C–O, 1.212 Å. The S–N bond is thus significantly longer than in sulfonylsulfilimines. The S–N bond in *S,S*-dimethyl-*N*-trichloroacetylsulfilimine is similar (1.667 Å), but the bond lengths in the trichloroacetylimido group indicate slightly higher charge density on oxygen: N–C, 1.320 Å, and C–O, 1.227 Å.[90]

C. Dipole Moments

Values of dipole moments for several *N*-tosylsulfilimines[91] and for three *N*-arylsulfilimines[92] are given in Table XIII. By comparison with dimethyl sulfoxide (μ = 4.3 D) the tosylsulfilimine is more polar, and the arylsulfilimines are less polar. The dipole moments of the chlorophenylsulfilimines are also lower than those of the corresponding chloroanilines, the difference being greatest for the *p*-chloro compounds (for *p*-chloroaniline μ = 3.36 D). The moment of the aryl carbon–nitrogen bond thus appears to be directed in the opposite sense to that of the carbon–chlorine bond in the sulfilimine; this is rationalized as being due to the coplanarity of the S–N aryl system in arylsulfilimines, the interaction of the nitrogen lone pair with sulfur preventing its interaction with the aromatic π system.[92]

D. Photoelectron Spectra

The x-ray photoelectron spectrum of *S*-benzyl-*S*-methyl-*N*-tosylsulfilimine has been measured.[93] The binding energy of the sulfonium sulfur atom (166.6 eV) shows that the SN bond is about 45% covalent, compared with 60% for the corresponding sulfoxide. The greater polarity of the SN bond is ascribed to the inductive stabilization of the negative charge on nitrogen by the tosyl group.

E. Infrared Spectra

Most sulfilimines show one or more strong absorption bands in the range 800–1150 cm^{-1}, which have been ascribed to the SN stretching frequency. Values are given in Table XIV for representative types.

Arenesulfonylsulfilimines show four characteristic bands at 1280–1260, 1140–1130, 1090–1070, and 1012–930 cm^{-1}, the first two of which are associated with stretching vibrations of the SO_2 group.[13,94–97] It has been suggested that the lowest frequency band is the asymmetric S^{IV}–N–S^{VI} band.[97] The effects of varying the sulfur and arenesulfonyl substituents on the fre-

TABLE XIV. Infrared Frequencies of Sulfilimines Associated with the SN Bond

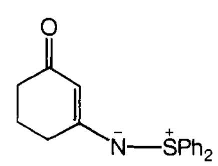
Sulfilimine	ν_{max}, cm^{-1} (SN)	Ref
$Ph_2S^+\bar{N}H$	910[a]	28
$Ph_2S^+\bar{N}H$, H_2O	940[b]	54
$Ph_2S^+\bar{N}Cl$	860	62
$Ph_2S^+\bar{N}Me$	1140, 1080[a]	28
$Ph_2S^+\bar{N}CH_2Ph$	1090, 1064[a]	28
$Ph_2S^+\bar{N}Ph$	930[a]	28
$Me_2S^+\bar{N}Ar$	920–890[a]	92
$R_2S^+\bar{N}CONH_2$	1040–960[b]	104
$Me_2S^+\bar{N}CO_2Et$	821, 782[c]	99
$Et_2S^+\bar{N}COCHCl_2$	825, 810[a]	101
$Me_2S^+\bar{N}COMe$	797[b]	100
$Ph_2S^+\bar{N}COPh$	805[b]	54
$Ph_2S^+\bar{N}C{=}NHNH_2$	840	9
$RR_2S^+\bar{N}SO_2Ar$	1012–930[a]	94, 95, 105
$Ph_2S^+\bar{N}SO_2Ar$	960[b]	54

[a] CCl_4 or $CHCl_3$ solution. [b] KBr disk. [c] Neat liquid.

quency of this band are very small, and no obvious trend is apparent. The band is at a similar position in cyclic arenesulfonylsulfilimines.[98]

N-Aryl-*S*,*S*-dimethylsulfilimines normally show three bands in the region 970–890 cm^{-1}; two of the three are assigned to deformations of the *S*-methyl groups, since similar bands are present in the spectrum of dimethyl sulfoxide.[92] The position of band at 920–890 cm^{-1}, associated with the SN bond, shows a small dependence on the nature of the substituent on the *N*-aryl group, electron-releasing substituents giving a slightly higher value. *S*,*S*-Dimethyl-*N*-mesitylsulfilimine has no well-defined absorption in this region; this may be because the bulk of the aryl group prevents it lying in the same plane as the SN bond.

Acylsulfilimines and related compounds generally show the SN stretching band at lower frequencies (790–830 cm^{-1}).[54,55,99-102] The splitting of the band which is observed in the spectra of some compounds of this type has been ascribed to their conformational mobility.[101] The carbonyl stretching frequencies provide good evidence for the delocalization of the negative charge: they are generally about 80–100 cm^{-1} lower than in the corresponding amides. For *N*-acetylsulfilimines the maximum is at 1570–1565 cm^{-1},[55,100] for *N*-benzoylsulfilimines values of 1595–1539 cm^{-1} have been reported,[54,55,102,103] and for *N*-ethoxycarbonyl derivatives, the frequency lies in the range 1630–1610 cm^{-1}.[54,55,99] The lowering of frequency is also seen in the vinylogous acylide **19** for which the carbonyl absorption is at 1595 cm^{-1}.[61] *N*-Carbamoyl ylides are exceptional in that the carbonyl frequency (1685–1640 cm^{-1}) is similar to that in urea.[104]



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F. Ultraviolet Spectra

Many arenesulfonylsulfilimines show two characteristic maxima in the ultraviolet region, one close to 230 nm (log ϵ 4.0–4.5) and the other near 270 nm (log ϵ 3.0–4.5).[25,91,95,105,106] *N*-Acyl- and *N*-ethoxycarbonylsulfilimines have a maximum at 217–231 nm (log ϵ 4.1–4.3);[55,99,100,106,107] the absorption has been found not to follow the Beer–Lambert law in some cases.[99,100]

There are four bands in the spectra of *N*-aryl-*S*,*S*-dialkylsulfilimines, at 210, 240–250 (log ϵ 3.6–4.0), 270–280 (log ϵ 3.75–4.05), and 315–325 nm (log ϵ 3.2–3.6); these spectra are interpreted as showing the existence of conjugation between the SN bond and the aromatic system.[92] As with the infrared spectrum, the ultraviolet spectrum of the *N*-mesitylsulfilimine is uncharacteristic, presumably because the aromatic ring is no longer coplanar with the SN bond.

G. Nuclear Magnetic Resonance Spectra

In the ^1H NMR spectra of *S*,*S*-dimethylsulfilimines the signal for the methyl group lies within a narrow range (δ 2.40–3.03), the exact value being determined by the electron-withdrawing capacity of the nitrogen substituent. In *N*-arylsulfilimines there is a slight but detectable shift of the signal to lower field as the aryl group becomes more electron-withdrawing.[16,92] The lowest value reported (δ 3.03) is for $Me_2S^+\bar{N}SO_2CF_3$.[108] Other values for $Me_2S^+\bar{N}R$ are: R = Ts, δ 2.68;[109] R = CO_2Et, δ 2.71;[99] R = COPh, δ 2.76;[103] and R = $COCHCl_2$, δ 2.80.[82] The S-methyl signal for *S*,*S*-dimethyl-*N*-tosylsulfilimine remains as a singlet at least down to −45 °C, despite the asymmetry of the ylide in the crystal, because of rotation about the SN bond (see section III.A). Dimethylsulfilimine, $Me_2S^+\bar{N}H$, has an abnormally high field signal for the methyl groups (δ 2.05),[110] but the role of water in the structure of this ylide is uncertain.

NMR has been used to determine the preferred conformations of some sulfilimines; these results are described in section III.A.

H. Mass Spectra

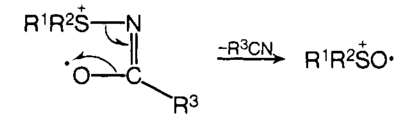
N-Aryl-*S*,*S*-dimethylsulfilimines show a strong molecular ion in the mass spectrum, but the base peak is invariably the $(M - 15)^+$ peak corresponding to the loss of a methyl group.[16,26] Other fragment ions are usually found at $(M - 30)^+$ (loss of two methyl groups), $(M - 61)^+$ (loss of $MeSCH_2$), $(M - 62)^+$ (loss of Me_2S), $(M - 76)^+$ (loss of Me_2SN), and $(M - 47)^+$ (loss of MeS). The last fragmentation must be preceded by a rearrangement, probably involving a methyl shift to nitrogen.

The primary mode of fragmentation of carbonyl-stabilized sulfilimines is cleavage of the group α to the carbonyl group.[55,99,100,111]

$$R^1R^2\overset{+\cdot}{S}\text{—}\dot{N}COR^3 \xrightarrow{-R^3\cdot} R^1R^2\overset{\cdot+}{S}NCO \xrightarrow{-NCO\cdot} R^1R^2S^{\ddagger}$$

R^3 = Me, Ph, OEt, NHPh

Another prominent peak in the spectra corresponds to the molecular ion of the sulfide, which may be derived directly from the molecular ion of the sulfilimine, or by stepwise loss of $R^3\cdot$ and $\cdot NCO$. If R^1 or R^2 are ethyl groups, loss of ethylene $(M - 28)^{+\cdot}$ is a major pathway for fragmentation.[100] Other major fragment ions in the spectra of *N*-benzoyl- and *N*-acetylsulfilimines corresponds to the sulfoxide ions, which may be formed through a four-membered ring transition state (eq 10).[55] Stevens rearrangement is suggested as a pathway in the mass spectral decomposition of *S*,*S*-dimethyl-*N*-acetyl- and -*N*-ethoxycarbonylsulfilimines.[99,100,111]



(10)

S,*S*-Diphenylsulfilimines show a strong $(M - SPh)^+$ peak, the base peak being 186 (Ph_2S) or 109 (PhS).[17,55] A major peak is also observed at *m/e* 200 (Ph_2SN).[59] *N*-Alkyl-*S*,*S*-diphenylsulfilimines undergo α-cleavage as the major fragmentation pathway (eq 11).[59]

$$Ph_2\overset{+}{S}\dot{N}CH_2R \xrightarrow{-R\cdot} Ph_2\overset{+}{S}N{=}CH_2 \qquad (11)$$

N-Arenesulfonylsulfilimines show additional fragmentation patterns corresponding to the loss of SO_2 and of R_2SNSO.[25]

IV. Chemical Properties

A. Basicity

The basicity of sulfilimines depends to a large extent upon the nature of the nitrogen substituents, and to a much smaller degree upon the nature of the sulfur substituents. The pK_a values of the free sulfilimines (Table XV) show that they are comparable in basicity to primary amines, whereas the arenesulfonylsulfilimines are very much weaker bases. The pK_a values of the sulfilimines $PhS^+Me\bar{N}SO_2Ar$ follow the order of the Hammett σ constants for the aryl substituents ($\rho = +0.82$) as do those in the series $ArS^+Me\bar{N}Ts$ ($\rho = +0.89$).[112] The acceptor properties of the group MeSNTs in the latter series are comparable to those of the methanesulfonyl group.[113]

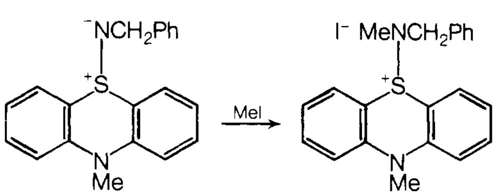
Free sulfilimines form isolable perchlorates,[65] hydrochlorides,[58] and *p*-toluenesulfonates.[54,56] Some *N*-acylsulfilimines also form isolable hydrochlorides,[24,99,100,102] but the reaction of anhydrous hydrogen chloride with *N*-alkyl-[28] and *N*-ethoxycarbonyl[8]-*S,S*-diphenylsulfilimines resulted only in isolation of decomposition products. Many sulfilimines form crystalline picrates, and these have proved to be particularly useful for purifying and characterizing hygroscopic or low-melting sulfilimines; picrates have been reported for free sulfilimines[58,114,115] and for aryl,[16,116] heteroaryl,[117] imidoyl,[12,17] phthalimido,[118] and sulfonyl[119] derivatives.

N-Aroyl-*S,S*-dimethylsulfilimines have also been shown to form stable crystalline complexes with Pd(II) and Pt(II) salts;[103,120] thus, *N*-benzoyl-*S,S*-dimethylsulfilimine and bis(triphenylphosphine)palladium dichloride gave the orange crystalline complex $[(PPh_3)_2PdCl_2 \cdot Me_2SNCOPh]$ in good yield. The carbonyl stretching frequency of the complex (1608 cm^{-1}) shows that coordination is through nitrogen.

B. Alkylation and Acylation

Alkylation and acylation of N-unsubstituted sulfilimines results in the formation of new sulfilimines: these reactions are described in section II.H.

N-Tosylsulfilimines are N-methylated by reaction with trimethyloxonium fluoroborate[78,121] or with methyl fluorosulfonate,[78] and are *N*-ethylated by triethyloxonium fluoroborate.[39a,121] Alkylation of *N*-alkylsulfilimines is easier; thus, the *N*-benzylsulfilimine **20** reacts rapidly with iodomethane,[65] and *S,S*-diphenyl-*N*-methylsulfilimine forms salts readily with iodomethane and with 2-iodopropane.[28]



20

Salts can also be isolated from the reaction of *S,S*-diphenyl-*N*-alkylsulfilimines with acid chlorides; for example, benzoyl chloride and *S,S*-diphenyl-*N*-methylsulfilimine react in dry ether to give the moisture-sensitive *N*-benzoylsulfonium salt in good yield.[28]

N-Acetyl- and *N*-benzoyl-*S,S*-dimethylsulfilimines undergo reactions with acetyl chloride and with acetic anhydride which are analogous to the Pummerer reaction of sulfoxides;[122] thus, the *N*-acetylsulfilimine reacts with acetyl chloride at 25 °C and with acetic anhydride at 70 °C to give, as major products, diacetamide (50–60%) and $MeSCH_2X$ (X = Cl or OCOMe) (48–63%).[123] The *N,N*-diacetylsulfonium salt **21** is postulated as an intermediate. *N*-Benzoyl-*S,S*-dimethylsulfilimine gives *N*-acetylbenzamide (44%) with acetic anhydride, probably by a similar mechanism.[21]

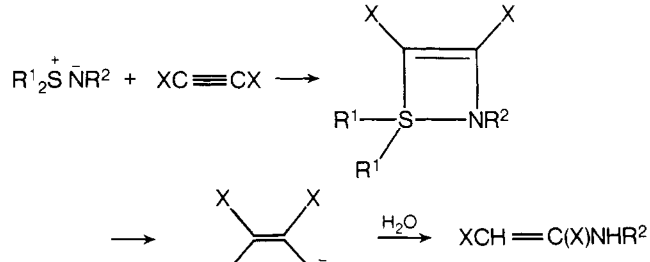
$$Me_2\overset{+}{S}\text{—}\overset{-}{N}COMe \xrightarrow{MeCOX} Me_2\overset{+}{S}\text{—}N(COMe)_2 \; X^- \longrightarrow MeSCH_2X + HN(COMe)_2$$

21

N-Tosylsulfilimines $PhS^+R\bar{N}Ts$ (R = Me, CH_2Ph, Ph) are quantitatively reduced to sulfides by reaction with acetyl chloride;[124] 2 mol of acetyl chloride is required, and chlorine is also formed. It is suggested that the *N*-acetylsulfonium salts rearrange to the *S*-chlorosulfonium salts $PhS^+RCl\ \bar{N}TsCOMe$ which are then attacked by a second mole of acetyl chloride.

The synthetically important nucleophilic addition reactions of sulfur-carbon ylides to electrophilic carbon centers have so far found relatively few parallels in sulfilimine chemistry. Reactions with simple carbonyl groups have not been observed, but addition to α,β-unsaturated carbonyl compounds has been reported both for N-unsubstituted[55,60] and for *N*-benzylsulfilimines.[59] In these reactions the sulfide is eliminated and formal "nitrene-transfer" products are isolated. These are of two types: aziridines and enamines. Two examples are shown in Scheme V.

With highly electrophilic acetylenes such as dimethyl acetylenedicarboxylate, nucleophilic addition occurs readily with



23

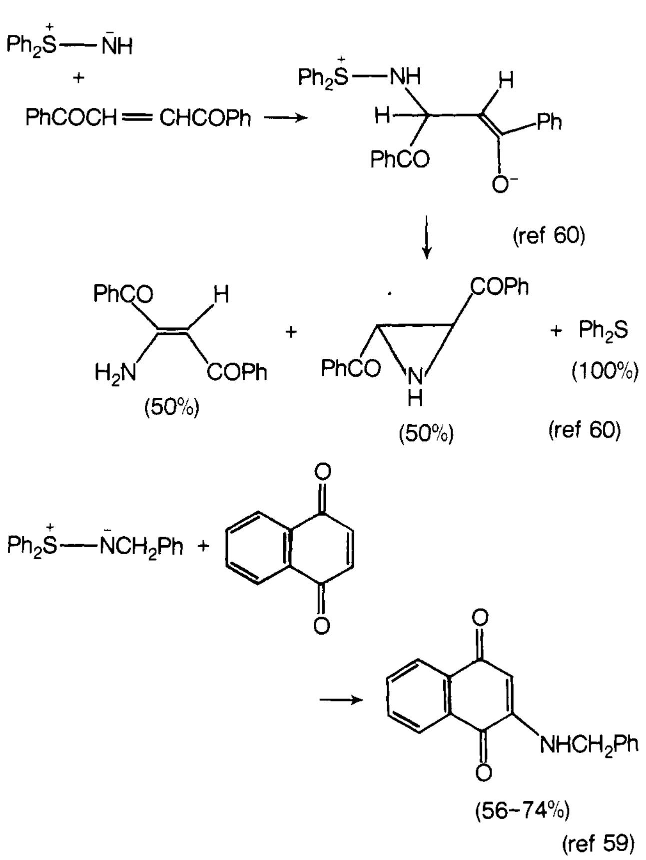
22

TABLE XV. Values of pK_a of Sulfilimines

Sulfilimine	pK_a	Ref
p-$MeC_6H_4S^+Ph\bar{N}H$	8.79	*a*
o-$MeC_6H_4S^+Ph\bar{N}H$	8.70	*a*
$Ph_2S^+\bar{N}H$	8.56	*a*
p-$ClC_6H_4S^+Ph\bar{N}H$	8.05	*a*
o-$NO_2C_6H_4S^+Ph\bar{N}H$	7.96	*a*
p-$NO_2C_6H_4S^+Ph\bar{N}H$	7.30	*a*
$Me_2S^+\bar{N}H$	7.28[b]	110
$Et_2S^+\bar{N}Ts$	4.70[b]	110
$Me_2S^+\bar{N}Ts$	0.57[c]	*d*
p-$MeOC_6H_4S^+Me\bar{N}Ts$	−1.78, −1.81	105, 112
$PhS^+Me\bar{N}SO_2C_6H_4$-p-OMe	−2.13	112
$PhS^+Me\bar{N}Ts$	−1.96,[c] −2.23	*d*, 112
m-$MeOC_6H_4S^+Me\bar{N}Ts$	−2.26	112
$PhS^+Me\bar{N}SO_2Ph$	−2.36	112
p-$ClC_6H_4S^+Me\bar{N}Ts$	−2.39	112
m-$ClC_6H_4S^+Me\bar{N}Ts$	−2.48	112
$PhS^+Me\bar{N}SO_2C_6H_4$-p-Cl	−2.55	112
m-$NO_2C_6H_4S^+Me\bar{N}Ts$	−2.85	112
p-$NO_2C_6H_4S^+Me\bar{N}Ts$	−2.93	112
$PhS^+Me\bar{N}SO_2C_6H_4$-p-NO_2	−3.00	112
$Ph_2S^+\bar{N}Ts$	−3.60[c]	*d*

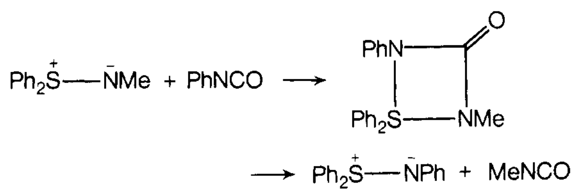
[a] N. Furukawa, T. Yoshimura, T. Omata, and S. Oae, *Chem. Ind. (London)*, 702 (1974). [b] Rate constants for hydrogen—deuterium exchange are also reported. [c] The procedure used to obtain these values has been criticized: D. Landini, G. Modena, G. Scorrano, and F. Taddei, *J. Am. Chem. Soc.*, **91**, 6703 (1969). [d] K. K. Andersen, W. H. Edwards, J. B. Biasotti, and R. A. Strecker, *J. Org. Chem.*, **31**, 2859 (1966).

SCHEME V



N-aryl-,[118,125] N-benzyl-,[59] and N-phthalimidosulfilimines.[118] The course of the reaction is the same in all cases and is analogous to the reaction of dimethyl sulfoxide with acetylenic esters.[126] The addition reaction appears to involve a four-center sulfurane intermediate, and the sulfide fragment is retained in the products, which are 1:1 adducts having the sulfonium ylide structures **22.** Products **23** arising from the hydrolysis of such intermediates are isolated in some cases, for example, with N-ethoxycarbonyl-S,S-dimethylsulfilimine.[125]

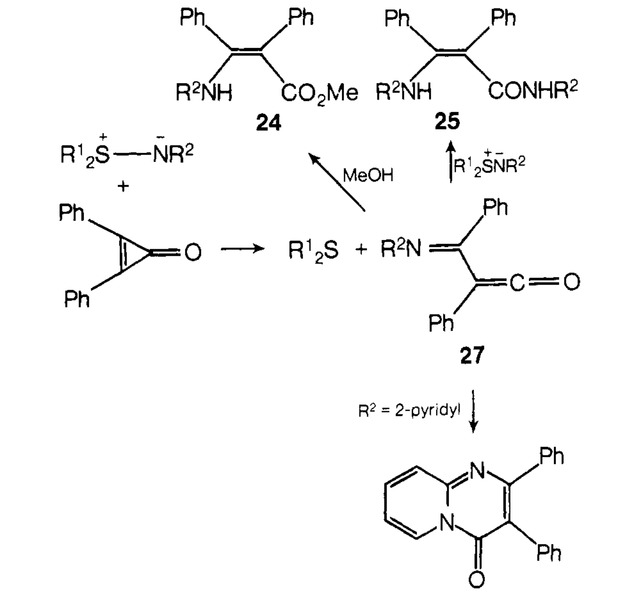
A somewhat similar mechanism can account for the "exchange" reaction between S,S-diphenyl-N-methylsulfilimine and phenyl isocyanate (eq 12).[28]



(12)

p-Tosyl isocyanate reacts with arenesulfonylsulfilimines in the presence of triphenylphosphine, all three components being required for reaction, giving arenesulfonylphosphinimines, triphenylphosphine oxide, and tosyl amide after hydrolysis.[31] These reactions appear to involve termolecular mechanisms similar to that shown in Scheme II for the conversion of sulfoxides into N-tosylsulfilimines.

Diphenylcyclopropenone is another highly electrophilic carbonyl compound which reacts with several sulfilimines. With N-aryl-[127] and with N-benzylsulfilimines,[59] diphenylcyclopropenone gives the enamines **24** and **25** in methanolic solution. S,S-Dimethyl-N-2-pyridylsulfilimine and related sulfilimines give simple 1:1 adducts (e.g., **26**) in good yields.[127] It is likely that these reactions involve ketene intermediates such as **27** which are intercepted either by the solvent or by internal nucleophiles.



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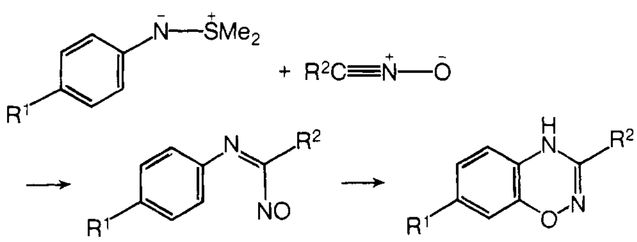
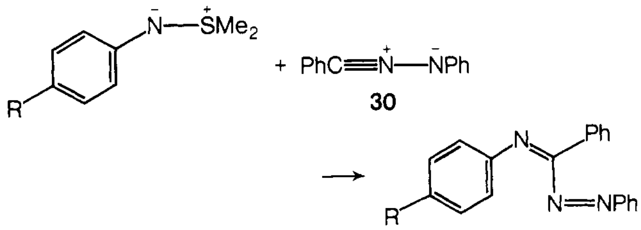
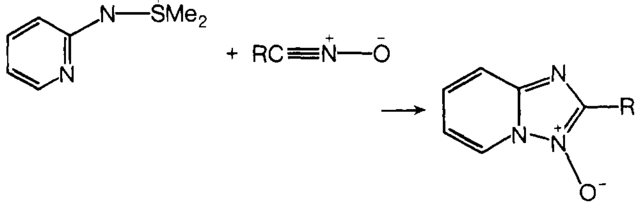
N-Aryl-S,S-dimethylsulfilimines also react with nitrile oxides at room temperature or below, giving 1,2,4-benzoxadiazines **28** in moderate yields.[128,129] In one such reaction (R^1 = Cl, R^2 = CO_2Et) a C-nitrosoimine intermediate **29** was intercepted as a



29 **28**



Diels–Alder adduct of the nucleophilic diene thebaine; in the absence of a diene, the intermediate undergoes electrocyclic ring closure to the 1,2,4-benzoxadiazine.[130] A similar reaction occurs with the nitrile imine **30**, but in this case the open-chain azoimine intermediate is stable enough to be isolated.[128]



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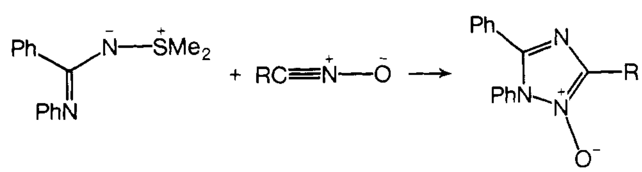
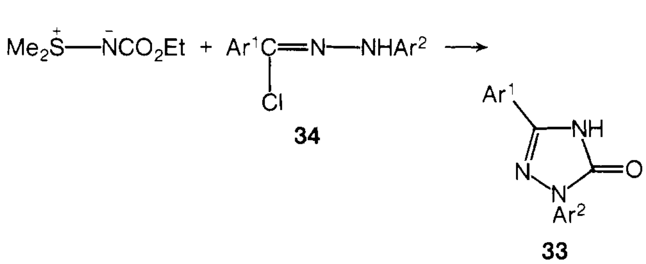


32

2-Pyridyl- and benzimidoylsulfilimines also react with nitrile oxides, and from these reactions, triazole *N*-oxides **31** and **32** have been isolated.[117] It is likely that *C*-nitrosoimines are also intermediates in these reactions,[130] but that they cyclize to give the aromatic five-membered ring products rather than six-membered ring isomers.

S,S-Dimethyl-*N*-ethoxycarbonylsulfilimine is reported to give triazolones **33** with α-chloro hydrazones **34**;[125] azoimine intermediates can also be invoked to account for the formation of these products.

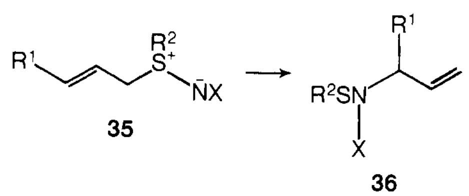


C. Thermal Reactions

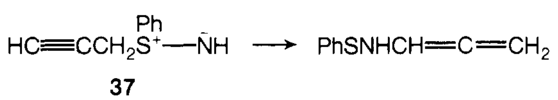
The type of reaction which occurs when a sulfilimine is heated depends to a large extent upon the nature of the substituents on sulfur. With *S,S*-diarylsulfilimines and with a few other systems a major reaction involves simple cleavage of the sulfur–nitrogen bond to give a sulfide, but in most cases the substituents on sulfur participate in the reactions.

1. S-Allylsulfilimines. [2,3] Sigmatropic Shifts

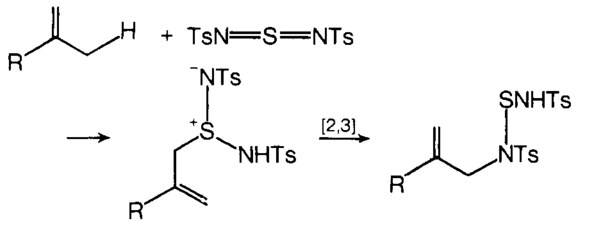
S-Allylsulfilimines (**35**, X = SO_2R) rearrange to sulfenamides **36** on mild heating, or slowly at room temperature.[131–133] The



reaction is first order and involves inversion of the allyl group,[131] as expected for an intramolecular [2,3] sigmatropic shift. Similar rearrangements occur spontaneously in *S*-allyl-*N*-phthalimidosulfilimines[134] and in the *S*-propargylsulfilimine **37**.[56]



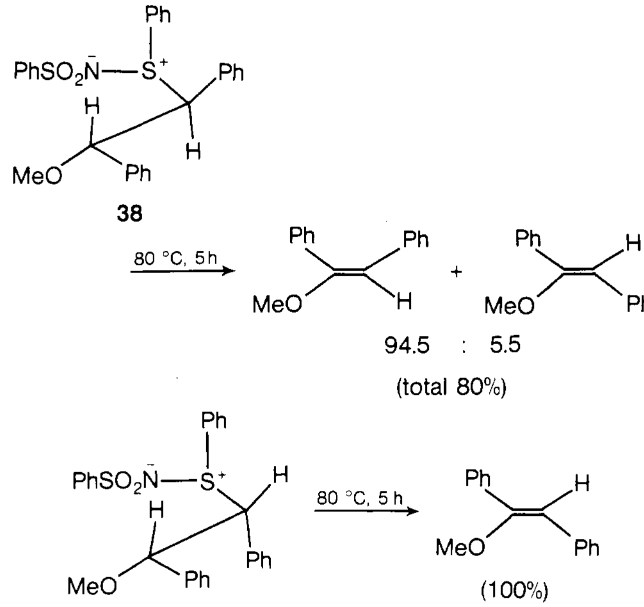
A variant of the reaction is used as a method of "allylic amination" of alkenes (eq 13).[135,136]

 (13)

2. S-Alkylsulfilimines with a β-Hydrogen Atom. Cycloelimination

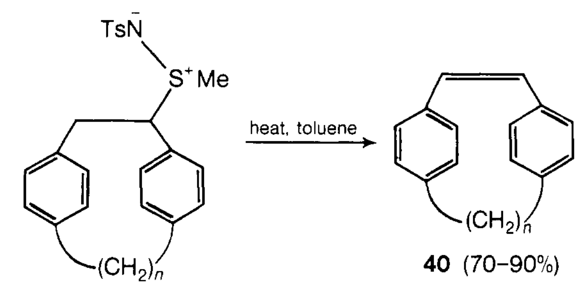
Sulfilimines bearing an *S*-alkyl group with a β-hydrogen atom commonly undergo an olefin-forming elimination reaction when they are heated at 80–150 °C. The mechanism of the reaction has been investigated with several *N*-arenesulfonylsulfilimines, and all the evidence points to a concerted syn (Ei) elimination (Scheme VI). Thus, the eliminations are first order with respect to sulfilimine and show a deuterium kinetic isotope effect[96,137]

SCHEME VI



(k_H/k_D = 3.03 at 80 °C for $PhS^+Et\bar{N}Ts$).[137] Change of solvent has relatively little effect on the reaction rate. The eliminations show high syn stereoselectivity, as illustrated for the threo and erythro isomers **38** and **39**.[138]

The ease of thermal syn elimination of these sulfilimines is greater than for the corresponding sulfoxides,[138,139] the stereoselectivity is slightly higher, and the yields of olefins are good, so that the reaction is a useful way of introducing double bonds. An example of its synthetic use is the production of [2,*n*]paracyclophan-(*n* + 7)-enes **40** from the corresponding *S*-methyl-*N*-tosylsulfilimines.[140]



40 (70–90%)

The direction of elimination in the sulfilimine **41** depends upon the solvent: in dimethyl sulfoxide or in the absence of solvent, Hofmann elimination to give 1-butene is the major reaction pathway, but in benzene 2-butene is the major product.[139]

$$EtCHMe\overset{+}{S}Ph\bar{N}Ts$$

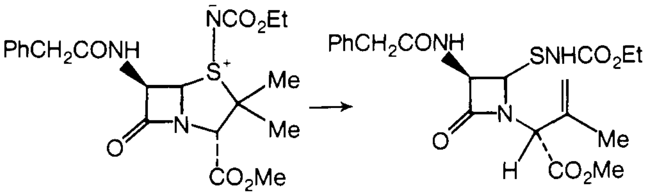
41

Similar cycloeliminations occur with appropriately S-substituted *N*-ethoxycarbonyl,[99] *N*-acetyl,[141] *N*-benzoyl,[102] *N*-carbamoyl,[104] and N-H[57] sulfilimines; for example, *N*-acetyl-*S,S*-diethylsulfilimine (**42**) gives ethylene and *N*-(ethylthio)acetamide when heated under reflux in xylene.[141] *N*-Arylsulfilimines normally undergo Sommelet–Hauser rearrangement as the major thermal process (see section IV.C.3), but those derived from sulfides bearing β-hydrogen atoms can also give cycloelimination products.[142]

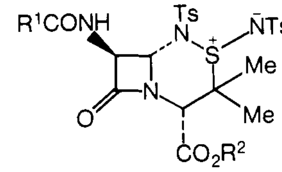
$$Et_2\overset{+}{S}—\bar{N}COMe \rightarrow CH_2{=}CH_2 + EtSNHCOMe$$

42 (51%) (95%)

An attempt to prepare the sulfilimine **43** by heating ethyl azidoformate with penicillin G methyl ester gave instead the elimination product **44** in low yield;[46] reaction of chloroamine-T



43 **44**



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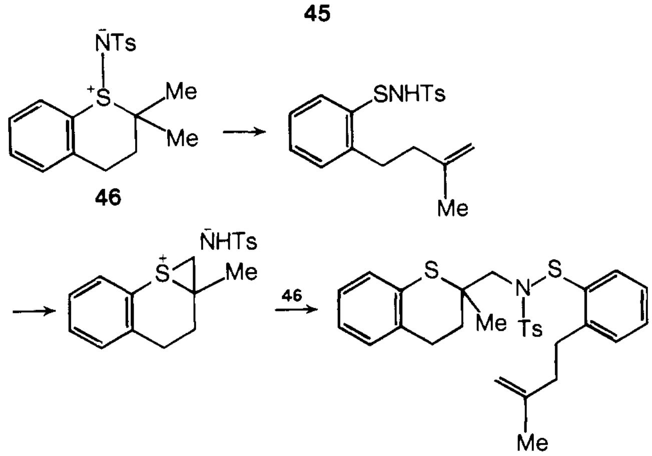


46 **47**

with penicillin esters resulted in the formation of 2:1 adducts **45** which underwent a similar cycloelimination when heated in toluene.[143] A related reaction takes place when the sulfilimine **46** is heated in benzene: cycloelimination is followed by a Pummerer rearrangement, leading to the formation of dimeric sulfenamide **47** in high yield.[144]

3. S-Alkylsulfilimines with an α-Hydrogen Atom. [1,2] Shifts and Sommelet-Hauser Rearrangements

A Pummerer-type rearrangement can occur with sulfilimines bearing an *S*-alkyl group with an α-hydrogen atom, the key step being the equilibration of the sulfilimine with an isomeric sulfonium ylide. A subsequent 1,2-shift of the nitrogen substituent to the carbanionic center gives **48**, the primary product of rearrangement.

$$R^1CH_2\overset{+}{S}R^2\overset{-}{N}X \rightleftharpoons R^1\overset{-}{C}H\overset{+}{S}R^2NHX \rightarrow R^2SCHR^1NHX$$

48

Good evidence for this mechanism comes from attempts to prepare *N*-tosylsulfilimines from sulfoxides containing activated methylene groups, by reaction of the sulfoxides with *N*-sulfinyltosylamide.[145] The sulfilimines were not isolated, but, from reactions performed at 35 °C, their products of Pummerer rearrangement **49** could be isolated in good yields. At 80 °C these products disproportionated to **50** and **51**.

$$TsNSO + MeSOCH_2R \rightarrow [RCH_2\overset{+}{S}Me\overset{-}{N}Ts]$$

$$\xrightarrow{35\ °C} MeSCHRNHTs \xrightarrow{80\ °C} (TsNH)_2CHR + (MeS)_2CHR$$

49 **50** **51**

R = PhCO, *p*-$MeOC_6H_4CO$, MeOCO, $C_5H_{11}CO$, CN

The primary products of Pummerer rearrangement **48** have not usually been isolated in other systems, although they are implicated as reaction intermediates. *N*-Benzyltosylamide is formed when the *N*-tosylsulfilimines **52** (R = Ph, CH_2Ph) are heated at 180-200 °C; the sulfilimine **52** (R = Me) is stable even at these temperatures.[132] Similarly, *N*-acetyl-*S,S*-dimethylsulfilimine decomposes at 120–125 °C to give, as major products, compounds **53** and **54**, which are almost certainly formed by a mechanism involving Pummerer rearrangement.[141]

$$PhCH_2\overset{+}{S}R\overset{-}{N}Ts \xrightarrow{180\ °C} RSCHPhNHTs \rightarrow PhCH_2NHTs$$

52

$$Me_2\overset{+}{S}\overset{-}{N}COMe \xrightarrow{120\ °C} MeSCH_2NHCOMe \rightarrow (Me_2S)_2CH_2$$

53 (62%)

$$+ (MeCONH)_2CH_2$$

54 (38%)

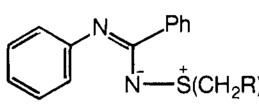
The reaction of *N*-aminophthalimide with *N*-chlorosuccinimide and dibenzyl sulfide gave *N*-(benzylideneamino)phthalimide (**55**) (95%) instead of the sulfilimine **56**, which was not detected.[19] A possible mechanism for this reaction also involves a [1,2] shift.

$$(PhCH_2)_2\overset{+}{S}\overset{-}{N}R \rightarrow PhCH_2SCHPhNHR \rightarrow PhCH{=}NR$$

56 **55**

R = phthalimido

When the *N*-arylbenzimidoylsulfilimines **57** were heated in solution at 190 °C, quinazolines **58** and triphenyl-*s*-triazine were isolated.[17] It is likely that these compounds are derived from the



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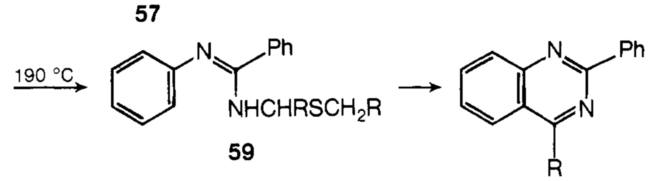
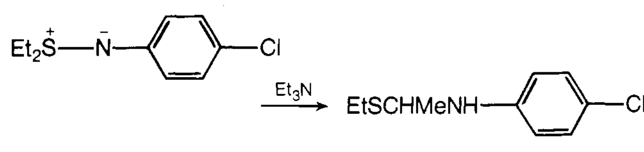


59 **58**

R = H (19%)
R = Ph (38%)

intermediates **59** since an attempted independent synthesis of **59** (R = H) gave the same final products.

A [1,2] shift is also reported when *N*-*p*-chlorophenyl-*S,S*-diethylsulfilimine is heated in cyclohexane with triethylamine; the aniline **60** is isolated in high yield.[146] Normally, however,

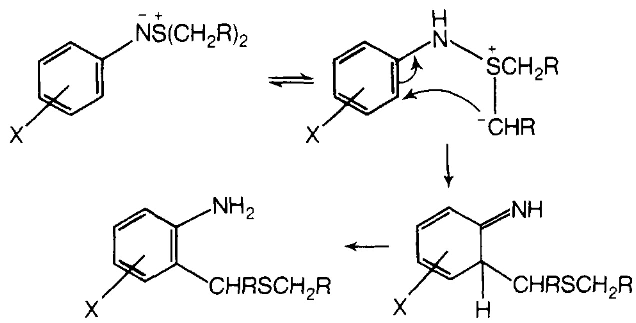


60 (98%)

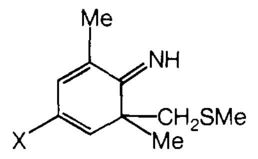
N-arylsulfilimines undergo a different type of rearrangement, the Sommelet-Hauser rearrangement, when heated in aprotic solvents with a base[22,146,147] or in protic solvents without a base.[146,147] This reaction (Scheme VII) also involves proton transfer from the α-carbon atom to nitrogen as a first step; an allowed [2,3] sigmatropic rearrangement of the resulting sulfonium ylide then leads to the formation of 2-substituted anilines.

The reaction has been shown to go in good yield with a wide range of *N*-arylsulfilimines, including compounds in which both ortho positions are blocked by methyl groups. From the latter

SCHEME VII

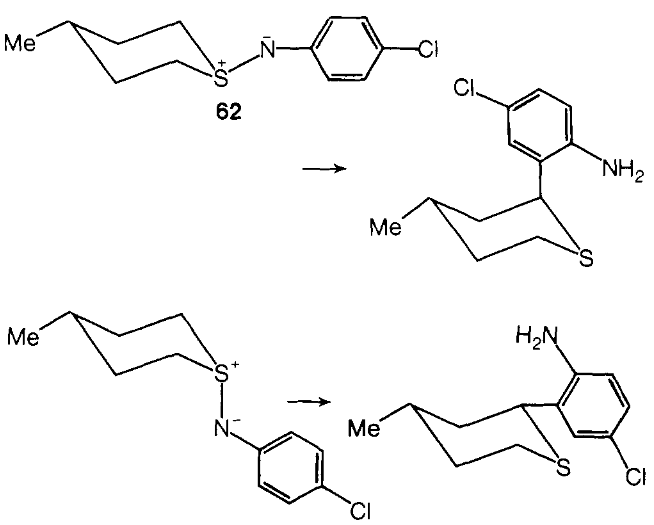


compounds the unstable 2,4-cyclohexadienone imines **61** were isolated.[146]



61

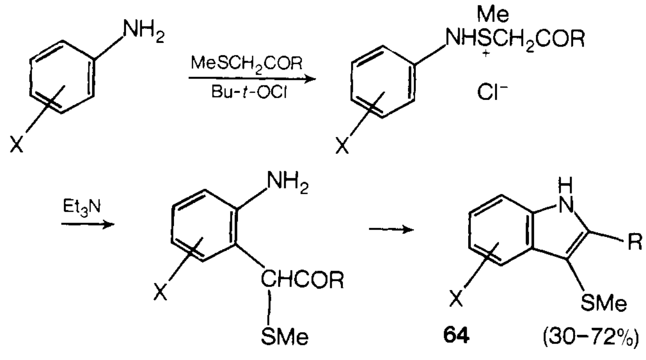
The rate of rearrangement depends upon the rate of proton abstraction from the *S*-alkyl group and upon the position of equilibrium for protonation on nitrogen; thus, the reaction shows a kinetic isotope effect (k_H/k_D for the rearrangement of *N*-*p*-chlorophenyl-*S,S*-dimethylsulfilimine and for the S,S-perdeuterated compound is 2.5–3.3), and the rate of rearrangement is decreased by electron-withdrawing para substituents.[147] The concertedness of the rearrangement has been demonstrated for the isomers **62** and **63**, which give only the products expected for a suprafacial [2,3] sigmatropic shift.[148]



62

63

The Sommelet–Hauser rearrangement has been developed by Gassman and his co-workers into a general method of ortho-alkylation of anilines. The sulfilimine is not normally isolated in their procedure; the aniline is converted in situ into an azasulfonium salt by reaction with *tert*-butyl hypochlorite and a sulfide, and the salt is then treated with a base to give the rearrangement product.[142] Synthetically useful extensions of the method include the alkylation of 2-aminopyridines at the 3 position,[149] the ortho-formylation of anilines by using 1,3-dithiane as the sulfide,[150a] and the formation of indoles **64** from anilines and *β*-keto sulfides.[150b]



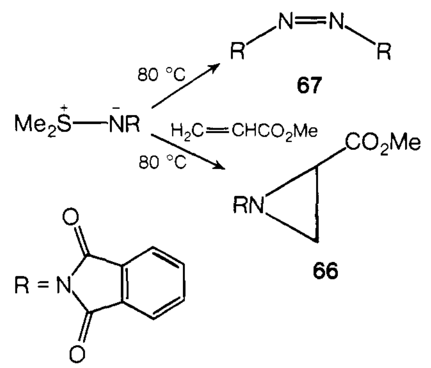
64 (30–72%)

4. Other Reactions

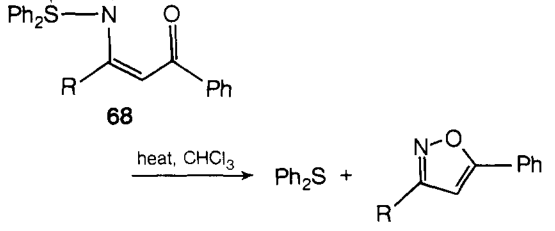
Sulfilimines unsubstituted on nitrogen give the corresponding sulfide, ammonia, and nitrogen when they are heated; several additional minor products have been detected in the decomposition of *S*-alkyl derivatives.[57,83,114] *S,S*-Diphenyl-*N*-methylsulfilimine decomposes to give diphenyl sulfide when it is heated at 175 °C.[28] *N*-Chloro-*S,S*-diphenylsulfilimine gives diphenyl sulfide and diphenyl sulfoxide, together with the salt **65**, in benzene and in other solvents.[62]

$$Ph_2\overset{+}{S}-\overset{-}{N}Cl \xrightarrow[\text{room temp}]{\text{benzene}} \underset{\mathbf{65}\ (74\%)}{[Ph_2S\cdots N\cdots SPh_2]^+Cl^-} + \underset{(12\%)}{Ph_2S} + \underset{(20\%)}{Ph_2SO}$$

There is good evidence that *S,S*-dimethyl-*N*-phthalimidosulfilimine gives phthalimidonitrene when it is heated at 80 °C. In the presence of olefins, aziridines, e.g., **66**, can be isolated in good yield, and in their absence, *cis*-phthaloyltetrazene (**67**) is a major product.[19] The tetrazene is also formed when *N*-aminophthalimide is oxidized in the presence of diphenyl sulfide, and *S,S*-diphenyl-*N*-phthalimidosulfilimine has been proposed as an intermediate in this reaction.[151]

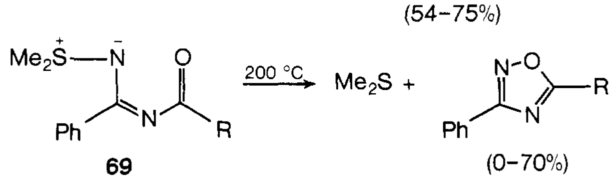


When the conjugatively stabilized sulfilimines **68, 69,** and **70** are heated, an intramolecular displacement of sulfide takes place and heterocyclic products are isolated.



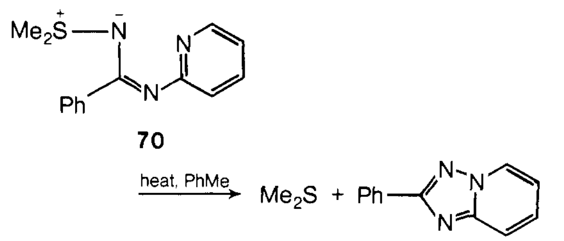
68

(54–75%) (ref 55)



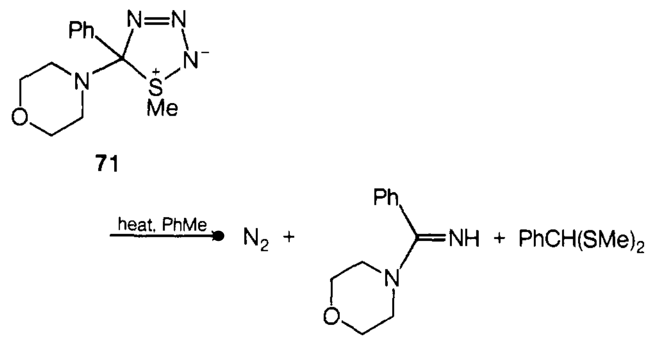
69

(0–70%) (ref 152)



70

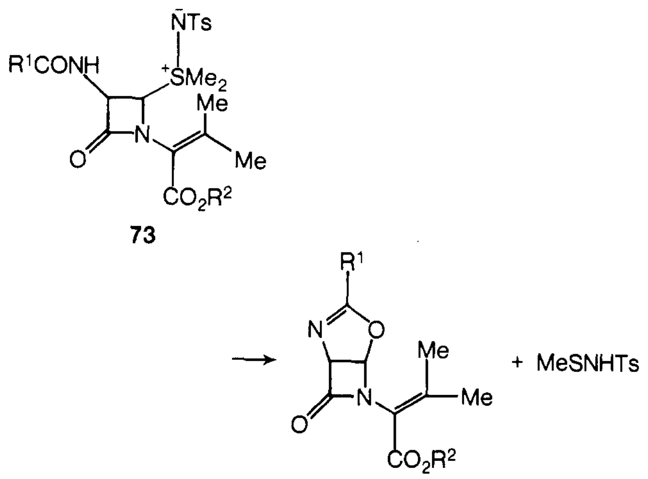
Nitrogen is eliminated from the cyclic sulfilimine **71** when it is heated at 80–105 °c. From its solution pyrolysis in toluene, the amidine **72** is isolated in high yield;[153] a radical mechanism for the decomposition seems likely.



71

72 (74%)

Pyrolysis of the β-lactam sulfilimines **73** in toluene gave the fused oxazolines **74**.[143b]



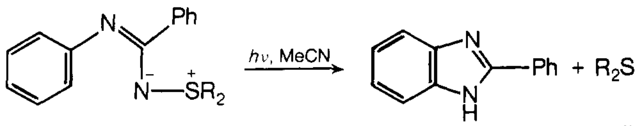
73

74

D. Photochemical Reactions

The known photochemical reactions of sulfilimines almost invariably involve cleavage of the sulfur–nitrogen bond. Where comparisons have been made, the reactions are found to be very similar to those of the corresponding azides. Thus, *N*-benzoyl-*S,S*-dimethylsulfilimine and benzoyl azide both form *N*-benzoylaziridines stereospecifically when irradiated in *cis*- and *trans*-4-methylpent-2-ene;[43] phenyl isocyanate is also produced. Singlet benzoylnitrene is proposed as the precursor of the *N*-benzoylaziridines. Photolysis of the sulfilimine in methanol gives benzamide (47%) and methyl *N*-phenylcarbamate (33%) as the major products.[24] *S,S*-Dimethyl-*N*-ethoxycarbonylsulfilimine and ethyl azidoformate also show very similar photochemical behavior.[44]

N-Arylbenzimidoylsulfilimines give benzimidazoles in high yield (eq 14) when they are irradiated in acetonitrile.[17] This reaction parallels the photochemical behavior of 1,5-diaryltetrazoles, which also give 2-arylbenzimidazoles. The similarity also extends to sulfilimines and tetrazoles in which the ortho position of the *N*-aryl group is blocked. Thus, the sulfilimine **75** and the tetrazole **76** both give as a photolysis product the pyrimidine **77**, which is probably derived from an intermediate 3a*H*-benzimidazole **78**, by a series of [1,5] sigmatropic shifts.[154]



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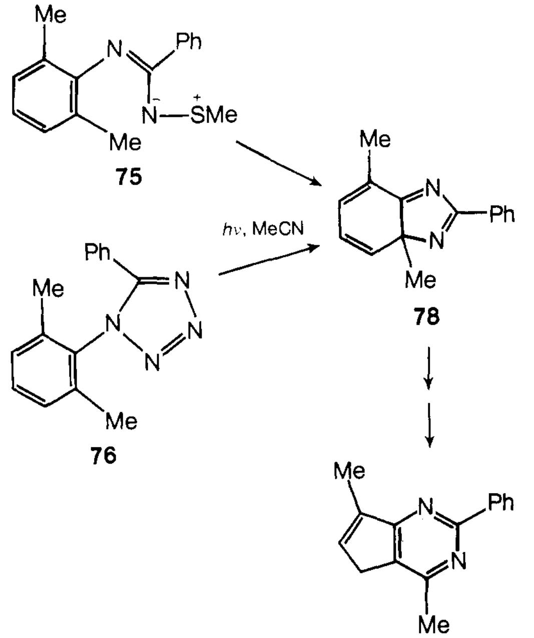


75

76

78

77 (13–17%)

Other examples of sulfur–nitrogen bond cleavage in the photolysis of sulfilimines are reported with *S,S*-diphenyl-*N*-methylsulfilimine[28] and with *S,S*-dimethyl-*N*-tosylsulfilimine.[25] The latter when irradiated in methanol gave *p*-toluenesulfonamide and ammonium *p*-toluenesulfonate as the major products.

E. Oxidation

Sulfilimines can be oxidized to the corresponding sulfoximines in good yields by reaction with potassium permanganate in basic or neutral media. Such reactions have been reported for N-unsubstituted sulfilimines[57] and for *N*-alkyl,[28] *N*-aryl,[16,116] *N*-acyl,[24,155] and *N*-arene sulfonyl derivatives. *N*-Tosylsulfilimines have also been converted into sulfoximines by their reaction with *m*-chloroperbenzoic acid.[35] The oxidation of *N*-arenesulfonylsulfilimines proceeds with retention of configuration at sulfur.[32,35,39a,156]

S,S-Diphenylsulfilimine reacts with chloramine-T in methanol at room temperature to give $Ph_2S^+(NH)\bar{N}Ts$ (54%) and $Ph_2S^+(O)\bar{N}Ts$ (39%).[157]

F. Reduction

A wide range of methods is available for the reduction of *N*-arenesulfonylsulfilimines to the corresponding sulfides. Catalytic hydrogenolysis is the established method;[158] this and other methods of reduction are summarized in Table XVI. The kinetics of the reduction by thiophenol are consistent with a mechanism involving fast reversible protonation of the sulfilimine followed by slow attack of thiophenoxide ion on the cation.[159] When potassium thiophenoxide is used as the reducing agent in dimethylformamide solution, a different reaction may occur with *N*-tosylsulfilimines bearing an *S*-alkyl group: this involves nu-

TABLE XVI. Methods of Reduction of *N*-Arenesulfonylsulfilimines

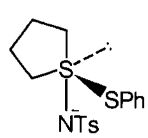
Reducing agent	Conditions	Yields, %	Ref
H_2	Pd, 1 atm, room temp	55–75	158
Sn/HCl aq	100 °C	73–95	132
$H_2NC{=}NH.SO_2H$	NaOH, $R_4P^+Br^-$, 70°	26–100	*a*
$(RO)_2PS_2H$	Room temp	~100	*b*
Bu_3SnH	AIBN, THF, reflux	30–40	*c*
$MeCS_2H$	Room temp	~100	*d*
NaI/$HClO_4$ aq	25 °C	~100	159, *e*
MeCOCl	Room temp	~100	124
PhSH	MeOH, room temp	~100	159

[a] G. Borgogno, S. Colonna, and R. Fornasier, *Synthesis*, 529 (1975). [b] S. Oae, A. Nakanishi, and N. Tsujimoto, *Tetrahedron*, **28**, 2981 (1972). [c] S. Kozuka, S. Furumai, T. Akasaka, and S. Oae, *Chem. Ind. (London)*, 496 (1974). [d] S. Oae, T. Yagihara, and T. Okabe, *Tetrahedron*, **28**, 3203 (1972). [e] C. Dell'Erba, G. Guanti, G. Leandri, and G. Poluzzi Corallo, *Int. J. Sulfur Chem.*, **8**, 261 (1973).

cleophilic attack by thiophenoxide ion on the α-carbon atom, giving an alkyl phenyl sulfide (eq 15).[160,161] The reaction has been shown to go with inversion of configuration at the α-carbon atom, as would be expected for an S_N2 process.[160]

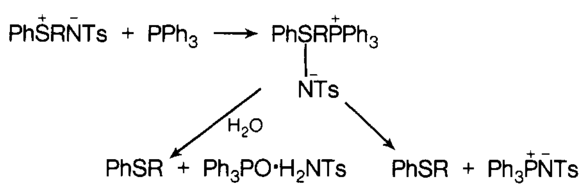
$$Ar\overset{+}{S}R\overset{-}{N}Ts + Ph\overset{-}{S} \xrightarrow[20-25\ ^\circ C]{Me_2NCHO} PhSR + ArS\overset{-}{N}Ts \xrightarrow{PhS^-} PhSSAr \quad (15)$$

It is likely that a four-covalent (sulfurane) intermediate is produced in systems where the initial nucleophilic attack is at sulfur. The sulfilimine $(CH_2)_4S^+\overset{-}{N}Ts$ reacts with thiophenolate ion to give tetrahydrothiophene in high yield;[160] here the structure of an intermediate sulfurane **79** would be particularly favorable,[162] with the five-membered ring bridging equatorial and axial positions.



79

Similar nucleophilic attack on sulfur probably occurs in the reduction of *N*-tosylsulfilimines by heating with cyanide ions in dimethylformamide or dimethyl sulfoxide[163-165] and in the reaction of *S*-phenyl-*N*-tosylsulfilimines with phosphines.[164,166a,167] The products derived from the tosylsulfilimine–phosphine system depend upon the conditions: the sulfide and *N*-tosylphosphinimine are produced in anhydrous dimethylformamide at 100–130 °C, but in the presence of water a phosphine oxide–tosylamide complex is formed (eq 16). The tosylsulfilimine–triphenylphosphine system can act as a dehydrating agent, converting carboxylic acids to anhydrides, and mixtures of an acid and an alcohol to the corresponding ester.[168]



(16)

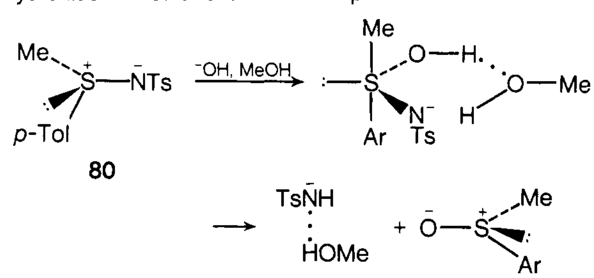
S,S-Diaryl-*N*-tosylsulfilimines also give good yields of diaryl sulfides in their reaction with arylmagnesium bromide[169] and aryllithium[166] derivatives; nucleophilic attack on sulfur to give a sulfurane intermediate again appears to be a likely first step. Triarylsulfonium chlorides have been isolated when the reaction mixtures are quenched with aqueous hydrochloric acid.[170]

Other reported reductions of sulfilimines include the catalytic hydrogenolysis of *N*-alkylsulfilimines[28] and the reaction of *N*-carbamoylsulfilimines with thiophenol.[104]

G. Hydrolysis and Other Reactions with Bases and Nucleophiles

Many of the reactions which result in the reduction of *N*-tosylsulfilimines (section IV.F) involve nucleophilic attack at sulfur to give a sulfurane intermediate. The reactions of this type can give a variety of products other than sulfides, depending upon the conditions. The reactions of *N*-tosylsulfilimines with thiophenolate anions illustrate another possible mode of attack of nucleophiles, that is, attack at the α-carbon atom of the *S*-alkyl group with displacement of the ion RS$\overset{-}{N}$Ts. A third type of reaction can take place with nucleophiles which are also good bases: the reagent can abstract a proton from the *S*-alkyl group, usually an α-proton. As a result of this variety of possible reaction pathways, the products of reaction of *N*-tosylsulfilimines with nucleophiles are very sensitive to the nature of the substituents on sulfur, the reaction conditions, and the structure of the nucleophile.

The variety of possible reactions is illustrated by the action of methanolic potassium hydroxide on different *N*-tosylsulfilimines. The chiral sulfilimine **80** is hydrolyzed to methyl *p*-tolyl sulfoxide by reaction with a saturated solution of potassium hydroxide in methanol at room temperature.[35] The reaction goes

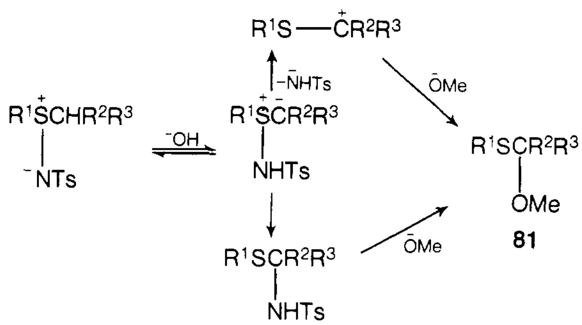


(17)

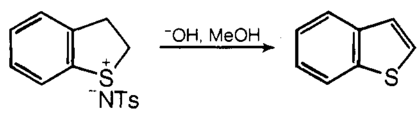
in good yield and with high stereoselectivity, leading to the formation of the sulfoxide of inverted configuration. Cram and his co-workers have proposed that an intermediate sulfurane is formed in which both the incoming and leaving groups occupy equatorial positions (eq 17); this allows intramolecular proton transfer to take place.

A later investigation by Furukawa, Oae, and their co-workers has shown that high yields of sulfoxides are obtained from *N*-tosylsulfilimines and methanolic potassium hydroxide only in exceptional cases.[171,172] Diaryl *N*-tosylsulfilimines do not normally react, whereas dialkyl or alkyl aryl derivatives give the sulfoxides and the α-methoxy sulfides **81** as the major products, the latter being favored by sulfilimines with bulky *S*-alkyl substituents. The mechanism proposed by the authors for the formation of the α-methoxy sulfides involves α-proton abstraction, elimination of tosyl amide anion to give a sulfur-stabilized carbonium ion, and attack by methoxide.[171] Alternatively, the reaction can be formulated as a rearrangement, followed by nucleophilic displacement of tosyl amide anion by methoxide (Scheme VIII).

SCHEME VIII

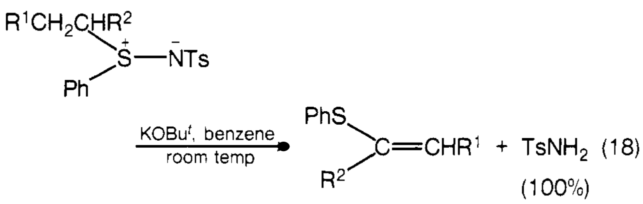


The cyclic sulfilimine **82** gives benzothiophene with potassium hydroxide in methanol;[32] here, elimination of tosyl amide from the product of rearrangement is favored, since the final product is aromatic.



82

A similar reaction takes place when acyclic *N*-tosylsulfilimines with a β-hydrogen atom are treated with potassium *tert*-butoxide in benzene; vinyl sulfides are produced in useful yields (eq 18).[173]



R^1	R^2	Yield, %
H	H	27
Me	H	60
H	Me	80
$-(CH_2)_4-$		83
H	Ph	76

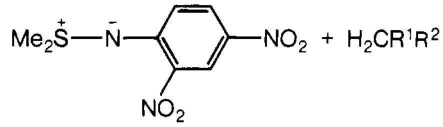
Chloride ion can also function as a nucleophile which attacks the α-carbon atom of *N*-tosylsulfilimines. When *S*-methyl-*S*-phenyl-*N*-tosylsulfilimine is heated with lithium chloride in a dipolar aprotic solvent, *N*-methyltosylamide and diphenyl disulfide are formed in high yield.[174] The kinetics of the reaction are consistent with a rate-determining attack of chloride ion at the S-methyl group, followed by alkylation of the sulfenamide ion; the chloride ion therefore acts as a catalyst for the decomposition.

$$Ph\overset{+}{S}Me\overset{-}{N}Ts + Cl^- \xrightarrow{Me_2SO,\ 110\ ^\circ C} PhS\overset{-}{N}Ts + MeCl$$

$$\rightarrow PhSNMeTs + Cl^- \rightarrow \underset{(93\%)}{TsNHMe} + \underset{(88\%)}{PhSSPh}$$

N-Arenesulfonylsulfilimines can be hydrolyzed in acidic conditions.[20,32,35,175] A kinetic study of the reaction has shown that in most cases the rate-determining step is nucleophilic attack by water on the protonated sulfilimine.[175] Other types of sulfilimines may be hydrolyzed in acidic, basic, or neutral conditions, depending upon the nature of the nitrogen substituent. N-Unsubstituted- and *N*-alkyl-*S,S*-diphenylsulfilimines have been hydrolyzed with aqueous acid,[28] and *N*-carbamoylsulfilimines by warming in acidic, basic, or neutral solution.[104] *N*-Acetyl-*S,S*-dimethylsulfilimine is slowly hydrolyzed in water at 20 °C.[141]

S,S-Dimethyl-*N*-(2,4-dinitrophenyl)sulfilimine (**83**) undergoes a series of ligand exchange reactions when it is heated with malononitrile and similar activated methylene compounds in dimethylformamide;[68] the products are sulfonium ylides (eq 19). The reaction is most successful when the pK_a of the attacking nucleophile is lower than that of 2,4-dinitroaniline. Even *S,S*-dimethyl-*N*-tosylsulfilimine undergoes the exchange reaction to some extent (12%) with malononitrile.



83

$$\xrightarrow{Me_2NCHO,\ 90\ ^\circ C} Me_2\overset{+}{S}-\overset{-}{C}R^1R^2 + ArNH_2 \quad (19)$$

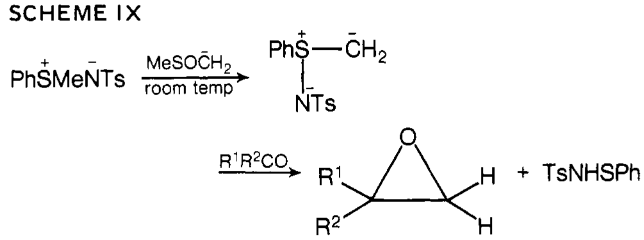
R^1	R^2	Yield, %
CN	CN	98
COMe	COMe	94
COMe	COEt	80
CO_2Me	CO_2Me	58
CO_2Et	CO_2Et	45

H. Miscellaneous Reactions

1. Reactions of S-Alkyl Substituents

In addition to those reactions described in earlier sections, there are a few reactions of tosylsulfilimines which primarily occur at the *S*-alkyl substituents. *S*-Alkyl-*S*-phenyl-*N*-tosylsulfilimines undergo hydrogen–deuterium exchange in aqueous dioxane containing sodium hydroxide; the rates of exchange are, surprisingly, greater than for the corresponding sulfoximines.[176] The anions of these sulfilimines can also be generated in anhydrous conditions using dimsylsodium, and they undergo carbanion transfer to aldehydes, ketones, and Schiff bases.[177] The reactions are illustrated in Scheme IX with examples of methylene transfer using *S*-methyl-*S*-phenyl-*N*-tosylsulfilimine.

SCHEME IX



R^1	R^2	Yield, %
Ph	H	61
Ph	Me	60
$-(CH_2)_5-$		57

N-Tosyl-*S*-vinylsulfilimines undergo conjugate addition to the vinyl group with a wide range of nucleophiles (eq 20).[178]

$$Ts\overset{-}{N}R\overset{+}{S}CH{=}CH_2 + BH \rightarrow Ts\overset{-}{N}R\overset{+}{S}CH_2CH_2B \quad (20)$$

2. Reaction with Dimethyl Sulfoxide

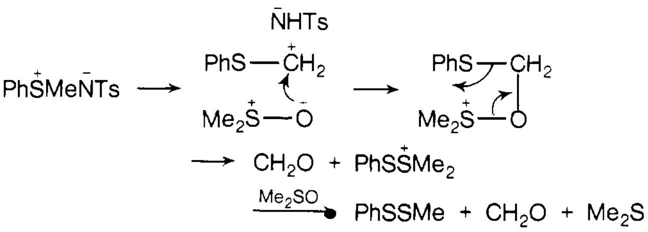
S-Methyl-*S*-phenyl-*N*-tosylsulfilimine and several related sulfilimines react with dimethyl sulfoxide at 180 °C.[179] The major products are disulfides and aldehydes derived from the *S*-alkyl group by oxidation. Diphenyl-*N*-tosylsulfilimine does not react.

$$Ph\overset{+}{S}Me\overset{-}{N}Ts \xrightarrow[180\ ^\circ C,\ 6\ h]{Me_2SO} \underset{(40\%)}{PhSSMe} + \underset{(30\%)}{PhSSPh} + \underset{(33\%)}{CH_2O}$$

$$(PhCH_2)_2\overset{+}{S}\overset{-}{N}Ts \xrightarrow[180\ ^\circ C,\ 3\ h]{Me_2SO} \underset{(37\%)}{PhCH_2SSMe} + \underset{(99\%)}{PhCHO}$$

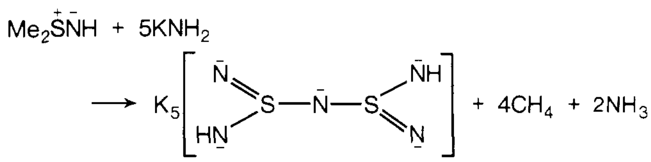
The mechanism proposed for the reaction involves the thermal elimination of TsNH and the attack of the sulfoxide, via oxygen, at the α-carbon atom (Scheme X).

SCHEME X



3. Reaction with Potassamide

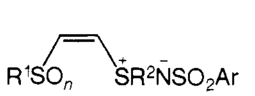
N-Unsubstituted *S,S*-diethyl- and *S,S*-dimethylsulfilimines form potassium salts with potassamide in liquid ammonia below 0 °C.[180] When the dimethylsulfilimine salt is heated in an autoclave at 110 °C with an excess of potassamide in ammonia, potassium pentaazadisulfite (**84**) is obtained, together with methane (90%).



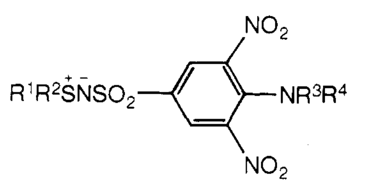
84

V. Uses

Herbicidal activity has been reported for arenesulfonylsulfilimines having the general structures **85**[181] and **86**,[182] and for *N*-cyanosulfilimines.[49]

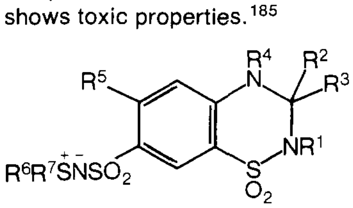


85

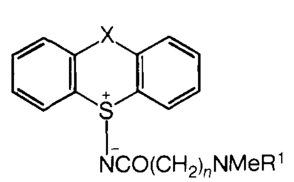


86

Sulfilimines which are claimed to have physiological activity include those of the general structure **87**, which show diuretic, natriuretic, and hypotensive properties,[183] and compounds related to **88**, which are antidepressants and stimulants of the central nervous system.[184] Bis(2-chloroethyl)-*N*-tosylsulfilimine is reported to be an inhibitor of tumor growth,[133] although it also shows toxic properties.[185]



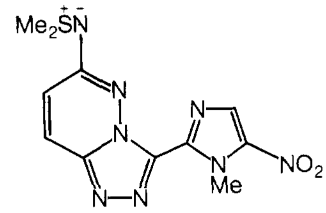
87



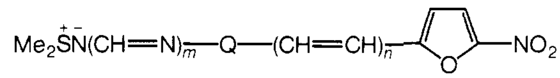
88

Several arenesulfonylsulfilimines with an amino or substituted amino group at the 4 position have shown activity against *streptococcus* species.[186] Sulfilimines which are reported to be useful antimicrobial agents include **89**[187] and compounds of the type **90**, where Q is a heteroaromatic group.[23]

N-Unsubstituted sulfilimines[187] and *N*-arenesulfonyl derivatives[188] are useful as antioxidants for plastics.



89



90

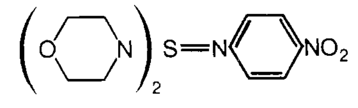
VI. Related Compounds

Compounds of the type XYS═NR, in which either or both of the groups X and Y are attached to sulfur through a heteroatom, are described briefly in this section. Examples of the most important groups of such compounds are shown in Table XVII. They have been subjected to relatively little systematic investigation, but their known reactions are not usually those characteristic of sulfilimines, the major reaction being nucleophilic displacement of the substituents attached to sulfur. Some of these compounds are, however, commonly named as sulfilimines, as indicated in Table XVII. Two classes will be considered: those based on imidosulfurous acid, in which both X and Y are attached to sulfur through a heteroatom, and sulfinimidic acid derivatives, in which one sulfur substituent is bonded through a carbon atom. The known six-membered heterocyclic analogues of these systems are also described.

TABLE XVII. Compounds Related to Sulfilimines

Formula	IUPAC name
$(OH)_2S{=}NH$	Imidosulfurous acid[a]
$(NH_2)_2S{=}NH$	Imidosulfurous diamide[b]
$F_2S{=}NH$	Imidosulfurous difluoride[a]
$Cl_2S{=}NH$	Imidosulfurous dichloride[a]
$Ph(NH_2)S{=}NH$	Benzenesulfinamidine[b]
$Ph(Cl)S{=}NH$	Benzenesulfinimidoyl chloride[a]

[a] Names of derivatives in *Chemical Abstracts* are usually based on these parent names. [b] Derivatives of these compounds are usually indexed as sulfilimines in *Chemical Abstracts*: thus, compound **91** is named as *S,S*-dimorpholino-*N*-*p*-nitrophenylsulfilimine and **92** is *S*-dimethylamino-*S*-phenyl-*N*-*p*-tolylsulfonylsulfilimine.



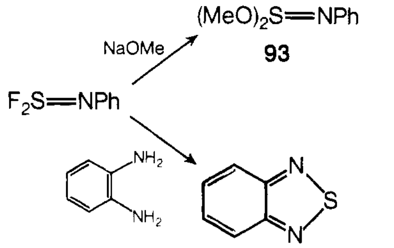
91

$Ph(NMe_2)S{=}NTs$

92

A. Imidosulfurous Acid Derivatives

The best known derivatives of imidosulfurous acid are the imidosulfurous dihalides, particularly the difluorides and dichlorides. Their chemistry has been reviewed by Levchenko and Markovskii,[189] and a survey of the most important methods for their preparation has been presented by Roesky.[190] For imidosulfurous difluorides, most preparations use sulfur tetrafluoride with an amine or amide,[191,192] or with a derivative such as an isocyanate,[66,193] *N*-trimethylsilylamine,[194] or phosphinimine.[195] Few reactions of imidosulfurous difluorides with organic substrates have been reported: they are readily hydrolyzed and react with nucleophiles with displacement of fluoride. Thus, *N*-phenylimidosulfurous difluoride gave the dimethyl ester **93** with sodium methoxide and 2,1,3-benzothiadiazole (**94**) with *o*-phenylenediamine.[66] With primary amines, sulfurdiimides RN═S═NR are formed.[192]



94

A general method of preparation of imidosulfurous dichlorides involves the reaction of a substance containing an NH_2 group with sulfur dichloride. Good yields of products are obtained with arylamines,[196,197] aminopyridines,[197] amides,[197] tertiary alkylamines,[198] and with stabilized primary enamines $(CN)_2C{=}C(X)NH_2$.[199] An improved procedure for *N*-acyl derivatives uses imidate esters with sulfur dichloride.[200] Chloramine-T and *N,N*-dichloroamines or -amides also give imidosulfurous dichlorides with sulfur dichloride, and with sulfur in the presence of a Lewis acid.[201] An alternative synthesis of these compounds uses the reaction of sulfinylamines, RNSO, with phosphorus pentachloride.[202,203]

The chemistry of these compounds is governed by the ready displacement of chloride by other nucleophiles. They are readily hydrolyzed, and reaction with secondary amines or *N*-trimethylsilylamines results in the replacement of one or both chlorides by amino groups (eq 21).[203,204]

$$Cl_2S{=}NR^1 \xrightarrow{R^2_2NH} Cl(R^2_2N)S{=}NR^1 \xrightarrow{R^2_2NH} (R^2N)_2S{=}NR^1 \quad (21)$$

An alternative synthesis of *N*-arenesulfonylimidosulfurous diamides, $(R_2N)_2S{=}NSO_2Ar$, is the reaction of the appropriate sulfide with an *N*-chlorosulfonamide.[205] Sulfur diimides are formed in the reaction of imidosulfurous dichlorides with primary amines.[198,203]

Examples are reported of the reaction of imidosulfurous dichlorides with aldehydes and with dimethylformamide, in which imines are formed together with thionyl chloride (eq 22 and 23).[40,199]

$$Cl_2S{=}NC(Cl){=}C(CN)_2 + RCHO \rightarrow RCH{=}NC(Cl){=}C(CN)_2 + SOCl_2 \quad (22)$$

$$Cl_2S{=}NAr + Me_2NCHO \rightarrow Me_2NCH{=}NAr + SOCl_2 \quad (23)$$

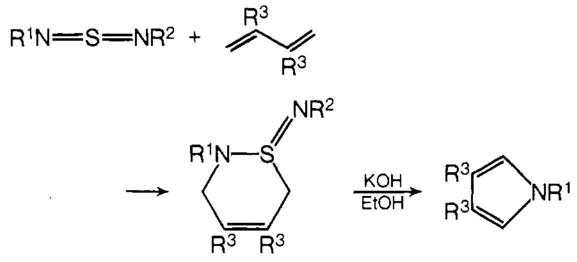
B. Sulfinimidic Acid Derivatives

Compounds of the type RS(NHTs)=NTs are readily available from the reaction of chloramine-T with thiols[206,207] or with a variety of thiol derivatives RSX (X = COR^1,[206,207] SR^1,[207,208] SO_2R^1,[209] Cl,[210] and $(EtO)_2PO$[210]). Chloramine-T also reacts with various N-substituted sulfenamides (eq 24);[211] *N*-haloamides[212] and *N*-bromoamidines[213,214] react in a similar manner.

$$R^1SNHR^2 + TsNNaCl \rightarrow RS(NHR){=}NTs + NaCl \quad (24)$$

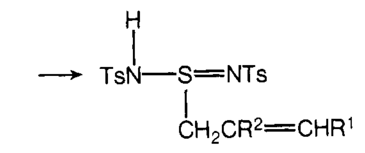
Sulfurdiimides have been found to undergo 1,4-cycloaddition with dienes (eq 25)[204,215] and the ene reaction with monoenes (eq 26),[41,135] both of which lead to the formation of sulfinamidines. The cyclic sulfinamidines **95** have been used as a source of α-free pyrroles,[215] while the allylic sulfinamidines **96** undergo rearrangement and elimination on further heating (see eq 13).

Arenesulfinimidoyl chlorides, Ar(Cl)S=NR, can be prepared from thiols[216] or from their trimethylsilyl derivatives[217] with *N,N*-dichloroamides; sulfenyl chlorides and disulfides have also been used as precursors.[218] Their reaction with amines provides an alternative route to sulfinamidines (eq 27).[219] Displacement of chloride by sulfur nucleophiles has also been observed.[220]



95 (25)

TsN=S=NTs + $R^1CH_2CR^2{=}CH_2$

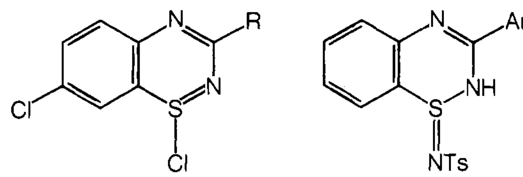


96 (26)

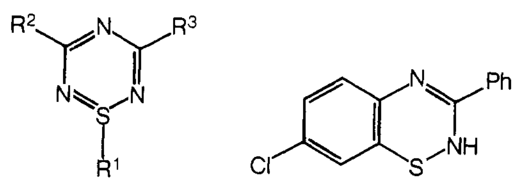
$$Ar^1(Cl)S{=}NSO_2Ar^2 + R^1R^2NH \rightarrow Ar^1(NR^1R^2)S{=}NSO_2Ar^2 + HCl \quad (27)$$

C. Benzo-1,2,4-thiadiazines and 1*H*-1,2,4,6-Thiatriazines

Two groups of cyclic ylides which incorporate the same structural features as the compounds described above are the benzo-1,2,4-thiadiazines **97** and **98** and the 1*H*-1,2,4,6-thiatriazines **99.** Compounds **97** are prepared by the reaction of *N*-arylamidines with sulfur dichloride or by chlorination of **100.**[221] The chlorine atom attached to sulfur can be displaced by morpholine. The related benzothiadiazines **98** are also prepared from *N*-arylamidines, by reaction with di-*N*-tosylsulfurdiimide or with *N*-tosylsulfinylamine.[222]



97, R = CCl_3, Ph, $C_6H_3Cl_2$ **98**



99 **100**

1,3,5-Trichloro-1,2,4,6-thiatriazine (**99,** $R^1 = R^2 = R^3 = Cl$) is the product of the reaction of sodium dicyaniimide with thionyl chloride;[223] other thiatriazines can be prepared from this compound by successive displacement of chloride by nucleophiles.[224] Other syntheses of 1,2,4,6-thiatriazines (R^1 = alkyl or aryl) are based on the reactions of *N*-bromoamidines with thiol salts and with sulfenamidines.[214,225]

Both groups of these cyclic ylides are readily hydrolyzed, and there is no evidence for aromatic character from their properties.[226]

VII. Addendum

X-Ray crystal structure determinations have been reported for three more sulfilimines: *S,S*-dimethyl-*N*-4-nitrophenylsulfilimine,[227] *N*-benzoyl-*S,S*-dimethylsulfilimine,[228] and the ylide **45**[229] derived from penicillin G methyl ester and chloramine-T.

The S–N bond length in the *N*-4-nitrophenyl ylide is short (1.651 Å) indicating that there is substantial double bond character. The structure of the *N*-benzoyl ylide is similar to that of other *N*-acylsulfilimines, with a S–N bond length of 1.659 Å and a planar SNCO system. The S–N bond length in the ylide **45** is 1.592 Å. Dipole moments have also been determined for a series of *N*-arylsulfilimines $4\text{-}XC_6H_4\bar{N}S^+Me_2$.[227] The values range from 5.53 D for the 4-fluoro derivative to 10.1 D for the 4-nitro derivative and are consistent with structures which have about 40–60% ionic character in the S–N bond. The value of 5.88 D for the 4-chloro derivative is much higher than that reported earlier for this compound.[92]

The preferred conformations of sulfilimines derived from thianes and 1,3-dithianes have been reinvestigated by NMR.[230] *N*-Tosyl-, *N*-4-chlorophenyl-, and *N*-benzoylsulfilimines derived from 1,3-dithiane all show a strong preference for the equatorial conformation, but of the corresponding thiane derivatives only the *N*-4-chlorophenylsulfilimine exists preferentially in the equatorial conformation. Rates of racemization[231] and absolute configurations[232] of a series of sulfilimines $MeOC_6H_4S^+Ph\bar{N}X$ have also been determined.

2-Substituted 1,3-dithianes and related compounds can be conveniently converted into the corresponding aldehydes and ketones by reaction with chloramine-T to give the corresponding sulfilimines, followed by hydrolysis.[233] If the 2-substituent bears a β-hydrogen atom, elimination takes place on reaction with base, and ketene thioacetals can be obtained in good yields.[234] Reaction of *N*-tosylsulfilimines derived from 2-unsubstituted 1,3-dithianes and related compounds with the nucleophiles RO^- and RS^- provides a route to triorthoformates.[235]

Sulfilimines form charge-transfer complexes with tetracyanoquinone, the strength of the interaction being related to the basicity of the sulfilimine.[236] This paper includes a brief description of a new method for preparing *N,S,S*-triarylsulfilimines, namely the reaction of the *N*-bromosulfilimines with aryllithium derivatives. A method of preparing sulfinimidoyl chlorides $RS{=}NR'Cl$ is the reaction of sulfenamides $RSNHR^1$ with chlorine and base.[237]

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