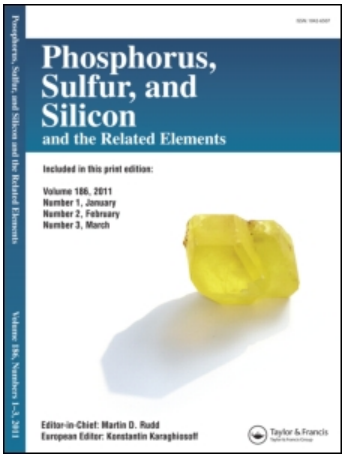

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CONVENIENT PREPARATION AND SPECTROSCOPIC STUDIES OF SULFOXIMINES AND SULFONEDIIMINES: *N*-CHLOROSULFILIMINE AS KEY INTERMEDIATE

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CONVENIENT PREPARATION AND SPECTROSCOPIC STUDIES OF SULFOXIMINES AND SULFONEDIIMINES: *N*-CHLOROSULFILIMINE AS KEY INTERMEDIATE

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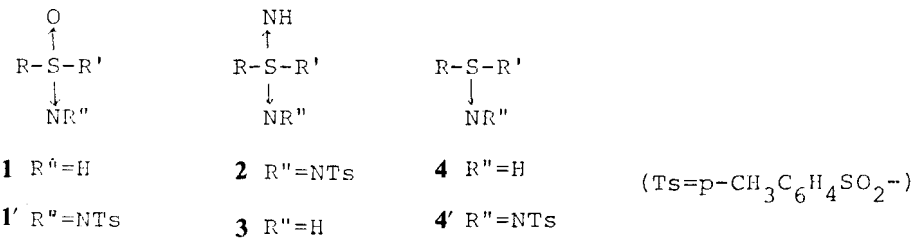
N-Unsubstituted sulfilimines, when reacted with sodium hypochlorite in an aqueous alkaline methanol solution or with Chloramine-*T* in dry acetonitrile in the presence of excess sodium salt of tosylamide were converted to the corresponding *N*-unsubstituted sulfoximines (**1**) or mono-*N*-tosylsulfonediimines (**2**) in good yields. **2** gave the unsubstituted sulfonediimines (**3**) in high yields upon treatment with conc. H_2SO_4. *N*-Chlorosulfilimine (**5**) was isolated in the initial stage of these reactions. **5** was found to react with NaOH in aqueous methanol and also with anhydrous Chloramine-*T* in dry acetonitrile to yield the corresponding **1** and **2** in good yields. IR, NMR, and Mass spectroscopic studies of **1**, **2**, and **3** were also carried out.

Both sulfoximines[1] and sulfonediimines[2] are aza analogues of sulfones and have interesting pharmacological properties.[3] However, their chemical reactivities have not been fully explored yet, except for a few scattered utilizations in organic syntheses, e.g., as alkylidene transfer reagents[4] and in the syntheses of heterocyclic sulfoximines.[5]

The following synthetic procedures of *N*-unsubstituted sulfoximines (**1**) have been reported; namely, (a) oxidation of *N*-unsubstituted sulfilimines (**4**),[6,7] (b) oxidative imination of sulfoxides,[8] (c) formation of sulfur–carbon linkages of sulfoximines,[9] and (d) desulfonylation of *N*-sulfonylsulfoximines (**1′**).[6,7] The last reaction is the simplest, since there is a convenient preparation of *N*-arenesulfonylsulfoximines (**1′**) which are easily converted to the corresponding **1** with conc. H_2SO_4 or Na in liq. NH_3, using sodium hypochlorite in ethyl acetate–water two phase system in the presence of a quaternary ammonium salt as catalyst.[10]



1 R"=H
1′ R"=NTs
2 R"=NTs
3 R"=H
4 R"=H
4′ R"=NTs

(Ts=p-$CH_3C_6H_4SO_2$-)

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Recently, Swern[11] and Johnson[12] also reported convenient methods to prepare *N*-arenesulfonylsulfoximine (**1'**) by treating the corresponding *N*-arenesulfonylsulfilimines (**4'**) with *m*-chloroperbenzoic acid (mCPBA) or hydrogen peroxide under alkaline condition. However, all other procedures have some drawbacks for large-scale preparation of various sulfoximines: e.g., it is difficult to prepare diarylsulfoximines directly from diarylsulfilimines; it is dangerous to use a large quantity of the toxic and explosive reagent, HN_3, in order to convert sulfoxides to sulfoximines. Recently, a simple procedure to prepare **4** has been found by us[6] and hence the direct oxidation of these **4** with $KMnO_4$ to afford the corresponding **1** in good yields has become quite convenient.[6,7] However, this reaction is also somewhat inconvenient for a large-scale preparation because of the formation of a large amount of precipitates containing mainly MnO_2. We have also reported a convenient one step reaction in one pot to prepare **1** in high yields by treatment of the corresponding **4** with sodium hypochlorite under alkaline conditions.[13]

Meanwhile, in the case of sulfonediimines, only a few methods to prepare dialkyl or alkyl aryl derivatives[14] involving reactions of sulfides with chloramine or of **4** with *tert*-butyl hypochlorite-ammonia have been reported. However, these methods cannot be satisfactorily applied to prepare diarylsulfonediimines. We have reported a convenient method to prepare *N*-mono-tosylsulfonediimines (**2**) and *N*-unsubstituted sulfonediimines (**3**) in good yields.[15]

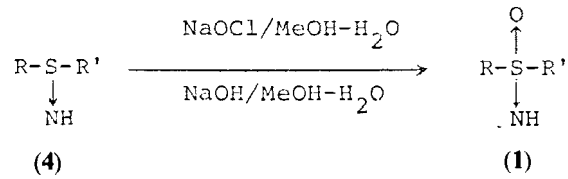
This paper summarizes the results of these convenient preparations as well as spectroscopic studies of sulfoximines (**1**), sulfonediimines (**2**), (**3**).

RESULTS AND DISCUSSION

Preparation of N-Unsubstituted Sulfoximines (**1**)

The sulfoxide is known to be oxidized with various oxidants to afford the corresponding sulfone.[16] However, it has been difficult to convert selectively the sulfilimine to the corresponding sulfoximine without oxidizing the imino group. The sulfilimine bearing an electron-withdrawing substituent such as *N*-tosyl group resists electrophilic oxidation.[11] On the other hand, the *N*-unsubstituted sulfilimine (**4**) is basic and the terminal imino group of **4** is more nucleophilic than the sulfinyl oxygen of the sulfoxide and most electrophiles attack the imino nitrogen to give the *N*-substituted sulfilimine or the reduction product, i.e., the sulfide. Therefore, many attempts have been made to achieve selective oxidation of **4** to **1**.

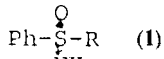
The reagent which we have successfully employed for the oxidation of **4** is commercially available sodium hypochlorite. The reagent oxidizes organosulfur compounds with only scant selectivity.[17] However, we were able to succeed in the oxidation of **4** to the corresponding **1** by treatment with sodium hypochlorite and then with sodium hydroxide in aqueous methanol as shown below. The results are listed in Table I.



(4) (1) (1)

TABLE I

Preparation of sulfoximine (**1**)

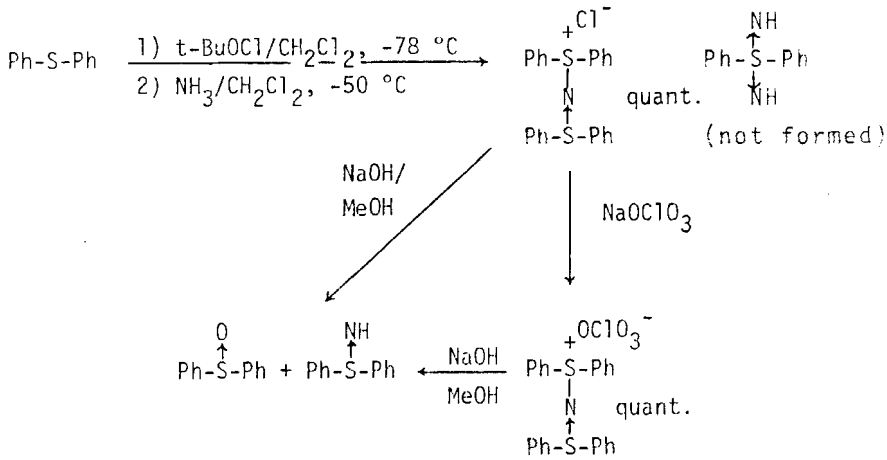


R	Yield (%)	mp (°C)	Analysis
1a C_6H_5	100	103.0 (lit. mp 104°C)[12]	
1b C_6H_4Cl-*p*	75	95.5–96.0	Calcd. for $C_{12}H_{10}NOSCl$: C, 57.25; H, 4.00; N, 5.56 Found: C, 57.18; H, 3.86; N, 5.59
1c $C_6H_4CH_3$-*p*	80	102.0–102.5 (lit. mp 101–102°C)[6]	
1d $C_6H_4NO_2$-*p*	85	159–159.5	Calcd. for $C_{12}H_{10}N_2O_3S$: C, 54.95; H, 3.84; N, 10.68 Found: C, 55.37; H, 3.73; N, 10.41
1e $C_6H_4OCH_3$-*o*	93	151.0–153.0 (lit. mp 149–150°C)[7]	
1h CH_3	71	34.0–35.0°C (lit. mp 34–35°C)[22]	

This elective oxidation of sulfilimines to sulfoximines with sodium hypochlorite is particularly useful since diarylsulfoximines, which are difficult to prepare by the usual methods,[18] are readily prepared by this method. The work-up is extremely simple and hence this procedure is a highly selective way of converting **4** to **1** under mild conditions.

Preparation of N-Mono-tosylsulfonediimines (**2**) *and N-Unsubstituted Sulfonediimines* (**3**)

We have reexamined first the reaction of diaryl sulfides with *tert*-butyl hypochlorite and ammonia in order to prepare sulfonediimines,[14] since dialkyl or alkylarylsulfonediimines have been prepared by this procedure, but no diarylsulfonediimines have been prepared by treatment of diaryl sulfide with *tert*-butyl hypochlorite and then with ammonia. When diphenyl sulfide was treated with *tert*-butyl hypochlorite and ammonia in the same way, the corresponding diphenylsulfiliminodiphenylsul-

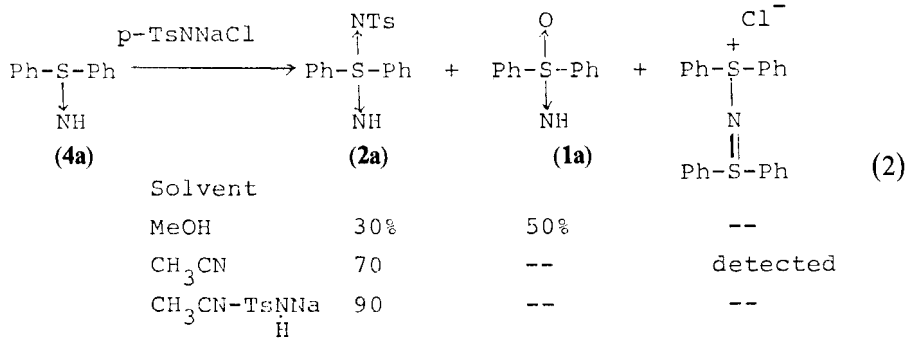


SCHEME 1 Reaction of diphenyl sulfide with *tert*-butyl hypochlorite and ammonia.

fonium chloride was obtained in a quantitative yield without formation of sulfonediimine. The whole reaction is shown in Scheme 1.

Attempts to prepare sulfonediimines by electrophilic oxidative imination either by treating **4** with hydrazoic acid in conc. H_2SO_4 or by treatment with *O*-mesitylenesulfonylhydroxylamine (MSH) in chloroform have been unsuccessful, affording no sulfonediimine. Nucleophilic oxidative imination by treatment of **4** or **4'** with MSH and sodium carbonate, as in the similar reaction with perbenzoate anion has also failed to afford the corresponding sulfonediimines.

The reagent which we have successfully employed for the oxidative imination of **4** is readily available Chloramine-*T*. When **4** was treated with Chloramine-*T* in methanol solution, both the corresponding **2** and **1** was obtained in 30% and 50% yields respectively. (Eq. (2))



(2)

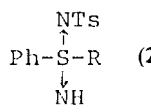
Separation of **2** and **1** was relatively difficult by the usual column chromatographic technique. However, upon treatment of the chloroform solution of **2** and **1** with 6N-HCl solution, the latter was preferentially dissolved into the aqueous solution and therefore, the mixture was separated nicely into the two components. When the above reaction was carried out in the presence of a large excess of TsNHNa, the yield of **2** increased to 40% though the concomitant formation of **1** could not be avoided due mainly to the contamination by water. Therefore, the reaction was conducted by using anhydrous Chloramine-*T* prepared from sodium salt of $TsNH_2$ and Cl_2 gas. However, even in such a treatment, **1** was obtained in 50% yield together with the desired **2** in 40% yield. Finally, when the reaction was carried out using the anhydrous **4** and anhydrous Chloramine-*T* in dry acetonitrile, **2** was obtained as a sole product in 70% yield. Meanwhile, the yield of **2** increased to 90% when a large excess of anhydrous TsNHNa was used. Although various solvents were tested for preparation of **2**, only acetonitrile and alcohol were found to be suitable for the preparation of **2** under the same conditions. By this simple procedure, several other diaryl-or alkylarylsulfonediimines have also been prepared successfully from the corresponding **4** in good yields. The results are summarized in Table II.

Preparation of N-Unsubstituted Sulfonediimines (**3**)

Sulfonediimines (**3**) were prepared by treatment of **2** with conc. H_2SO_4 at 35–40°C without any formation of such products as sulfoximines or sulfones. This process is

TABLE II

Preparation of *N*-tosylsulfonediimines (**4**)



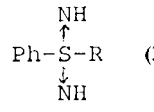
(**2**)

R	Yield (%)[a]	mp (°C)	Analysis
2a C_6H_5	90	153.0–153.5 (lit. mp 151.5–152.0°C)[16]	
2b C_6H_4Cl-*p*	80	124.0–124.5	Calcd. for $C_{19}H_{17}N_2O_2S_2Cl$: C, 56.36; H, 4.23; N, 6.92 Found: C, 56.32; H, 4.10; N, 6.80
2c $C_6H_4CH_3$-*p*	82	128.0–129.0	Calcd. for $C_{20}H_{20}N_2O_2S_2$: C, 62.47; H, 5.24; N, 7.28 Found: C, 62.71; H, 5.16; N, 7.23
2d $C_6H_4NO_2$-*p*	63	154.5–155.04	Calcd. for $C_{19}H_{17}N_3O_4S_2$: C, 54.93; H, 4.12; N, 10.11 Found: C, 54.74; H, 4.11; N, 9.83
2e $C_6H_4OCH_3$-*o*	31	171.0–172.0	Calcd. for $C_{20}H_{20}N_2O_3S_2$: C, 59.98; H, 5.03; N, 6.99 Found: C, 60.04; H, 4.99; N, 6.93
2f $C_6H_4CH_3$-*m*	88	122.0–123.0	Calcd. for $C_{20}H_{20}N_2O_2S_2$: C, 62.47; H, 5.24; N, 7.28 Found: C, 62.56; H, 5.12; N, 7.26
2g C_6H_4Br-*p*	70	125.5–126.0	Calcd. for $C_{19}H_{19}N_2O_2S_2Br$: C, 50.78; H, 3.81; N, 6.23 Found: C, 50.97; H, 3.77; N, 6.44
2h CH_3	44	162.0–163.0	Calcd: for $C_{14}H_{16}N_2O_2S_2$: C, 54.52; H, 5.22; N, 9.08 Found: C, 54.51; H, 5.11; N, 8.92
2i C_2H_5	45	105.5–106.0	Calcd. for $C_{15}H_{18}N_2O_2S_2$: C, 56.05; H, 5.22; N, 8.71 Found: C, 55.99; H, 5.59; N, 8.71

[a]Isolated yield.

TABLE III

Preparation of sulfonediimine (**3**)

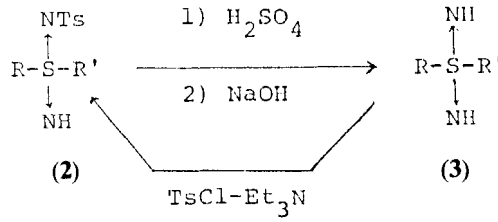


(**3**)

R	Yield (%)[a]	mp (°C)	Analysis
3a C_6H_5	100	91.0–92.0 (lit. mp 91–92°C)[15]	
3b C_6H_4Cl-*p*	100	128.0–129.0	Calcd. for $C_{12}H_{11}N_2SCl$: C, 57.48; H, 4.42; N, 11.17 Found: C, 57.51; H, 4.31; N, 11.15
3c $C_6H_4CH_3$-*p*	93	91.5–92.0	Calcd. for $C_{13}H_{14}N_2S$: C, 67.79; H, 6.12; N, 12.16 Found: C, 67.81; H, 6.08; N, 12.09
3d $C_6H_4NO_2$-*p*	95	185.0–185.5	Calcd. for $C_{12}H_{11}N_3O_2S$: C, 55.15; H, 4.24; N, 16.08 Found: C, 55.07; H, 4.05; N, 16.10
3f $C_6H_4CH_3$-*m*	100	92.0–93.0	Calcd. for $C_{13}H_{14}N_2S$: C, 67.79; H, 6.12; N, 12.16 Found: C, 67.81; H, 6.08; N, 12.09

[a]Isolated yield.

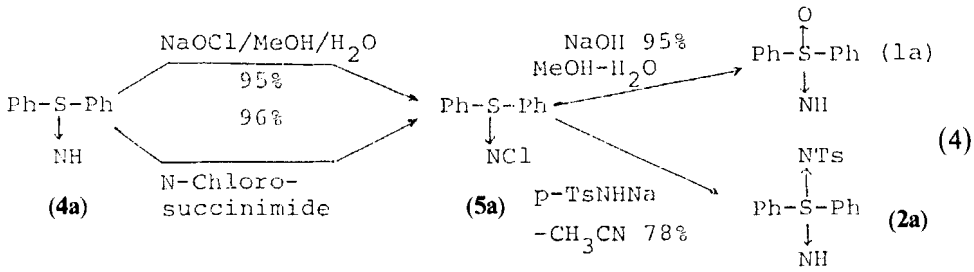
analogous to the method reported earlier by us to remove the sulfonyl group from **4**[6] and **1**[19] with conc. H_2SO_4. Transformation of **3** to **2** was achieved by treatment with *p*-toluenesulfonyl chloride in the presence of triethylamine, as shown in Eq. (3). These results are listed in Table III.



(3)

Isolation and Reaction of Diphenyl-N-chlorosulfilimine with Several Nucleophiles

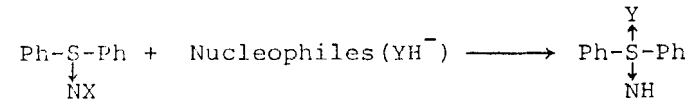
In the initial stage of both these reactions, i.e., preparation of **1a** (R=R′=Ph) and **2a** (R=R′=Ph), an intermediate, diphenyl-*N*-chlorosulfilimine (**5a**), was detected by TLC and HPLC analyses and actually isolated in good yield.[20] The intermediate (**5a**) readily reacted with NaOH in aqueous methanol and with anhydrous TsNHNa in dry acetonitrile to afford the corresponding **1a** and **2a** respectively. The reactions are shown in equation **4** and the results are summarized in Table IV.



(4)

TABLE IV

Reaction of *N*-halosulfilimines with nucleophiles



Nucleophile	X	Y	Solvent	Yield (%)[a]
NaOH	Cl	O	90% CH_3CN	90
NaOH	Cl	O	60% CH_3OH	95
NaOH	Br	O	60% CH_3OH	92
p-TsNHNa	Cl	NTs	dry CH_3CN	78
p-TsNHNa	Br	NTs	dry CH_3CN	76
n-$PrNH_2$	Cl	*N*-Pr-*n*	dry CH_3CN	54
n-$BuNH_2$	Cl	*N*-Bu-*n*	dry CH_3CN	43
NH_3	Cl	NH	dry CH_3CN	57
NH_3	Br	NH	dry CH_3CN	49

[a]Isolated yield.

Inspection of the data in the Table IV shows that the yields of **1a** or **2a** are nearly identical to those in the reaction of **4** with sodium hypochlorite in aqueous methanol under alkaline condition and those in the reaction with Chloramine-*T* in the presence of excess TsNHNa. The *N*-bromosulfilimine (**6**) also afforded the corresponding **1** and **2** in good yields under the same conditions. Both **5** and **6** also reacted with other nitrogen nucleophiles such as NH_3, propylamine and butylamine, to afford the corresponding sulfonediimines in 43–57% yields as shown in Table IV. These observations suggest that **5** is the key intermediate in both reactions of **4** with sodium hypochlorite and with Chloramine-*T* to afford the corresponding **1** and **2** respectively. The only side product obtained in the reaction as the sulfiliminosulfonium chloride which is considered to be formed by thermal decomposition of **5** under relatively mild conditions.

Our earlier stereochemical study on the reaction of optically active *S*-*o*-methoxyphenyl-*S*-phenyl-*N*-chlorosulfilimine with NaOH in aqueous methanol solution has revealed[21] that both the chlorination of **4** and the alkaline hydrolysis of **5** proceed with retention of configuration around the sulfur atom. The stereochemical study on the reaction of optically active *S*-methyl-*S*-*p*-tolylsulfilimine with Chloramine-*T* in liquid NH_3 was also shown[22] to proceed with retention of configuration around the sulfur atom. Since chlorination of the sulfilimine with Chloramine-*T* proceeds with retention of the configuration around the sulfur atom, the *N*-chlorosulfilimine **5** is considered to react with TsNHNa to give the monosulfonylsulfonediimine with retention of the configuration around the sulfur atom.

Spectroscopic Studies of Sulfoximines (**1**) *and Sulfonediimines* (**2**) *and* (**3**)

IR and NMR Spectra. IR and NMR spectra of sulfoximines (**1**) and sulfonediimines (**2**) and (**3**) are summarized in Tables V and VI.

Sulfoximines (**1**) have characteristic IR absorption bands in the ranges of 3260–3300(ν_{NH}), 1225–1245, 1120–1145, 1095–1100, and 980–990 cm^{-1} ($\nu_{asymNSO}$

TABLE V

IR and NMR of sulfoximine (**1**)

Sulfoximine	IR (cm^{-1}, KBr) ν_{NH}	IR (cm^{-1}, KBr) $\nu_{N=S=O}$	^{1}H-NMR[a]
1a	3260	1230, 1130, 1100, 1070, 985, 965	3.12 (1 H, s, —N—H), 7.30–8.18 (10 H, m, aromatic protons)
1b	3270	1235, 1095, 1000, 980	3.14 (1 H, s, —NH), 7.26–8.10 (9 H, m, aromatic protons)
1c	3260	1225, 1120, 1095, 980	2.38 (3 H, s, C_6H_4—C$\underline{H}_3$-*p*), 3.08 (1, H, s, NH), 7.20–8.17 (9 H, m, aromatic protons)
1d	3300	1245, 1145, 1095, 1075 990, 965	3.30 (1 H, s, NH), 7.27–8.27 (9 H, m, aromatic protons)
1e	3260	1280, 1250, 1230, 1120, 1120, 1090, 1020, 975	3.30 (1 H, s, NH), 3.68 (3 H, s, *o*-C$\underline{H}_3$O), 6.78–8.14 (9 H, m, aromatic protons)
1h	3230	1220, 1005, 990	2.92 (1 H, s, NH), 3.10 (3 H, s, *s*-C$\underline{H}_3$) 7.57–8.00 (5 H, m, aromatic protons)

[a] In $CDCl_3$ (TMS as internal standard).

TABLE VI

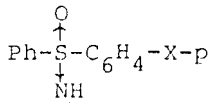
IR and NMR of sulfonediimine (**2**) and (**3**)

Sulfonediimine	IR (cm^{-1}, KBr) ν_{NH}	IR (cm^{-1}, KBr) $\nu_{N=S=N \text{ and } O=S=O}$	^{1}H-NMR[a]
2a	3270	1290, 1150, 1090, 1065, 1010	2.30 (3 H, s, $SO_2C_6H_4C\underline{H}_3$-*p*), 2.70 (1 H, s, NH), 7.00–8.10 (14 H, aromatic protons)
2b	3250	1300, 1160, 1090, 1040, 1010, 980	2.33 (3 H, s, $SO_2C_6H_4$—$C\underline{H}_3$-*p*), 3.00 (1 H, s, NH), 7.03–8.06 (13 H, m, aromatic protons)
2c	3150	1310, 1150, 1085, 1045, 1010, 980	2.33 (3 H, s, C_6H_4—$C\underline{H}_3$-*p*), 2.33 (3 H, s, $SO_2C_6H_4C\underline{H}_3$-*p*), 2.98 (1 H, s, NH), 6.98–8.00, 13 H, s, aromatic protons)
2d	3270	1305, 1160, 1090, 1040, 1010, 1000, 970	2.33 (3 H, s, $SO_2C_6H_4C\underline{H}_3$-*p*), 3.23, (1, H, s, NH) 7.21–8.21 (13 H, m, aromatic protons)
2e	3300	1305, 1155, 1085, 1065, 1045, 1020, 960	2.32 (3 H, s, $SO_2C_6H_4C\underline{H}_3$-*p*), 3.15 (1 H, s, NH) 3.48 (3 H, s, *o*-$C\underline{H}_3O$—), 6.70–8.30 (13 H, m, aromatic protons)
2f	3270	1320, 1155, 1090, 1080, 1035, 1010, 990	2.37 (3 H, s, *m*-$C\underline{H}_3$), 2.37 (3 H, s, $SO_2C_6H_4C\underline{H}_3$-*p*) 3.00 (1 H, s, NH), 7.07–8.14 (13 H, m, aromatic protons)
2g	3200	1300, 1140, 1080, 1030, 1000, 960	2.35 (3 H, s, $SO_2C_6H_4C\underline{H}_3$-*p*), 3.03 (1 H, s, NH), 7.07–8.13 (13 H, m, aromatic protons)
2h	3200	1300, 1140, 1080, 1030, 1000, 960	2.39 (3 H, s, $SO_2C_6H_4C\underline{H}_3$-*p*), 2.71 (1 H, s, NH), 3.37 (3 H, s, S—$C\underline{H}_3$), 7.13–8.13 (9 H, m, aromatic protons)
2i	3250	1300, 1150, 1080, 1050, 1000, 990	1.22 (3 H, t, $CH_2C\underline{H}_3$) 2.38 (3 H, s, $SO_2C_6H_4C\underline{H}_3$-*p*) 2.79 (1 H, s, NH), 3.47 (2 H, q, $C\underline{H}_2CH_3$) 7.13–8.10 (9 H, m, aromatic protons)
3a	3160	1130, 1090, 1065, 930	2.40 (2 H, s, NH), 7.15–7.50 (10 H, m, aromatic protons)
3b	3160	1140, 1095, 1065, 940	2.43 (2 H, s, NH), 730–8.21 (10 H, m, aromatic protons)
3c	3125	1130, 1100, 1065, 930	2.30 (2 H, s, NH), 2.30 (3 H, s, $C\underline{H}_3$-*p*), 7.03–8.00 (9 H, m, aromatic protons)
3d	3150	1140, 1100, 940	2.43 (2 H, s, NH), 690–8.30 (9 H, m, aromatic protons)
3f	3150	1130, 1090, 1045, 925	2.30 (2 H, s, NH), 2.36 (3 H, s, $C\underline{H}_3$-*m*), 7.25–8.26 (9 H, m, aromatic protons)

[a]In $CDCl_3$ (TMS as an internal standard).

TABLE VII

Major fragmentation peaks of sulfoximine (**1**)



(20 eV)

(**1**)

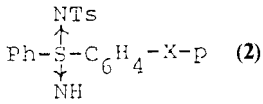
Peak X	NO_2	Cl	H	Me
parent	0.006	0.031	0.063	0.032
$[p\text{-X—}C_6H_4NHPh]^{+\cdot}$	0.031	0.016	0.128	—
$[p\text{-X—}C_6H_4SO]^{+\cdot}$	—	0.222	0.569	0.047
$[PhSO]^{+\cdot}$	1.000	0.297		0.022
$[p\text{-X—}C_6H_4NH]^{+\cdot}$	—	1.000	1.000	1.000
$[PhNH]^{+\cdot}$	0.950	0.600		0.041

and ν_{symNSO}), which are assigned to the stretching frequency bands of the N—H and NSO groups, respectively.[18] Sulfonediimines (**3**) have strong IR absorption bands at around 3125–3160 and 1130–1140, 1090–1100, and 930–940 cm^{-1}, which are ascribed to the N—H and NSN groups. *N*-Monotosyl-sulfonediimines (**2**) show strong absorption bands in the ranges of 3150–3300, 1290–1320, 1140–1160, 1080–1090, 1030–1065, and 955–990 cm^{-1}, which are assigned to the stretching bands of N—H, NSN and OSO groups.

The ^1H NMR spectra of sulfoximines (**1**) and sulfonediimines (**2**) and (**3**) show typical patterns similar to those of sulfones.[18] The chemical shift due to the imino

TABLE VIII

Major fragmentation peaks of sulfonediimine (**2**)

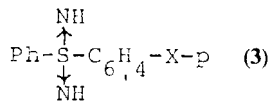


(**2**)

Peak X	NO_2	Br	Cl	H	Me	*m*-Me	*o*-OMe
$[PhSC_6H_4\text{—X-}p]^{+\cdot}$	0.118	0.103	0.067	0.119	0.076	0.152	0.040
$[PhNHC_6H_4\text{—X-}p]^{+\cdot}$	1.000	0.603	1.000	1.000	1.000	1.000	1.000
$[p\text{-}TsNH_2]^{+\cdot}$	0.388	0.150	0.298	0.179	0.152	0.172	0.210
$[p\text{-}C_6H_4NH]^{+\cdot}$	—	0.153	0.109	0.148	0.127	0.108	0.105
$[PhNH]^{+\cdot}$	0.223	0.097	—		0.049	0.081	0.094

TABLE IX

Major fragmentation peaks of sulfonediimine (3)



(3)

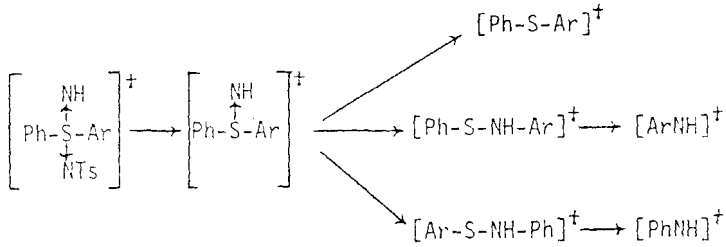
Peak X	NO_2	Cl	H	Me	*m*-Me
parent	0.013	0.044	0.059	0.084	0.075
$[PhSC_6H_4—X\text{-}p]^{+\cdot}$	0.019	0.050	0.025	0.047	0.106
$[ArS(N)NH]^{+\cdot}$	0.109	0.075	0.072	0.067	0.100
$[PhS(N)NH]^{+\cdot}$	0.184	0.097		0.063	0.069
$[ArSNH]^{+\cdot}$	0.088	0.344	0.616	0.413	0.322
$[PhSNH]^{+\cdot}$	1.000	1.000		0.278	0.325
$[ArNH]^{+\cdot}$	0.184	0.866	0.066	1.000	1.000
$[PhNH_2]^{+\cdot}$	0.063	0.563		0.141	0.250
$[ArNH]^{+\cdot}$	0.059	0.231	1.000	0.481	0.241
$[PhNH]^{+\cdot}$	0.850	0.906		0.438	0.603

proton appears nearly at the same position, regardless of the change of the groups attached to N—H group of **1**, **2**, and **3** respectively.

Mass Spectra. Mass spectroscopic analyses of a few diaryl sulfoximines and sulfonediimines were carried out at 20 eV by heating the inlet system at 180°C. Major fragmentation peaks are listed in Tables VII, VIII and IX.

Among major fragmentation peaks of diaryl sulfoximines (**1**) cited in Table VII, the parent peaks of all these sulfoximines (**1**) studied are obtained clearly at the corresponding mass peaks. Sulfoximines (**1**) gave a strong ion peak which is generated by migration of aryl group from the central sulfur atom to the imino nitrogen atom to form the corresponding aryl imido ion. The effect of substituents on aromatic ring in **1** was not observed in the mass spectra while the ion peak due to the corresponding aryl imide ion is generally a base peak except for the *p*-nitro compound. There is a clear peak, corresponding to $[ArPhNH]^+$ which is considered to be generated from the sulfinylarylphenylamide formed by migration of aryl or phenyl group from the sulfur atom to the nitrogen atom in the sulfinylanilide. This rearrangement, involving the migration of phenyl or aryl group from the sulfur atom to the imino nitrogen atom, is similar to that observed in the aryl migration from the sulfur atom to the imino nitrogen atom in the fragmentation of arylmethylsulfoximine and also to that of phenyl migration to an oxygen atom in the fragmentation of sulfones. Other important peaks are $[X—C_6H_4SO]^+$ and $[PhSO]^+$ which are derived from the corresponding sulfinylanilide.

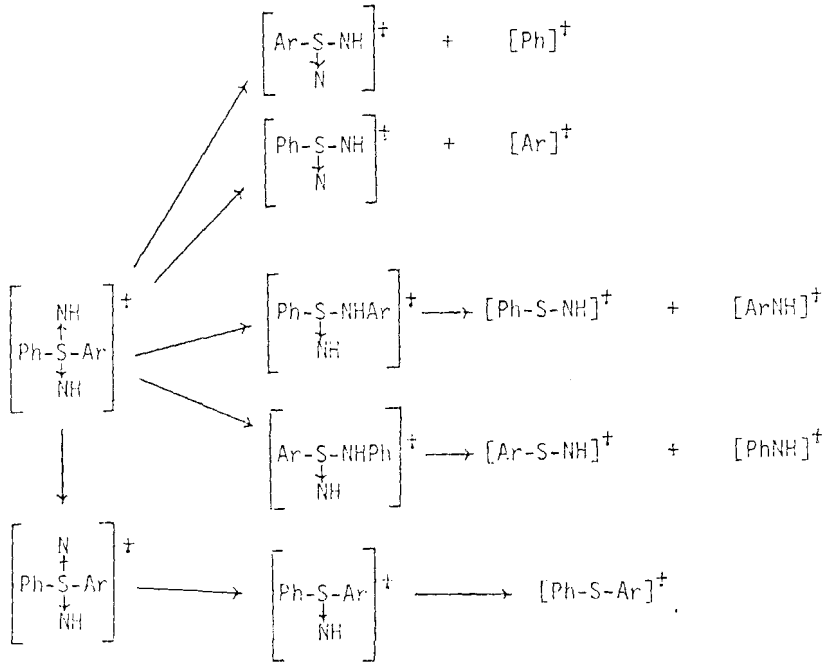
Major fragmentational peaks of sulfonediimines (**2**) are summarized in Table VIII. The parent peaks of **2** except for *S*-alkyl-*S*-aryl-compounds were not observed. The



SCHEME 2 Mass fragmentations of sulfonediimine (**2**).

base peaks observed are m/e = P-184, which correspond to the aryl sulfides. In addition to these, relatively intense peaks were observed at m/e; $[phS(NH)Ar]^+$, $[TsNH_2]^+$, and $[PhNH]^+$. These results suggest clearly that S—NTs bond is cleaved preferentially and $[ArNH]^+$ and $[PhNH]^+$ peaks are produced by facile migration of aryl group from sulfur atom to nitrogen atom. The migration of aryl group from the central sulfur atom to the imino nitrogen atom was also observed in the mass spectra of sulfoximines described above. Thus, the fragmentation of **2** may be illustrated in Scheme 2.

In contrast to the *N-mono-tosylsulfonediimines* (**2**), mass spectra of *N-unsub*stituted sulfonediimines (**3**) show a different fragmentation pattern; namely these compounds gave parent peaks at the corresponding molecular weight and base peaks which suggest that an aromatic ring migrates from the central sulfur atom to the imino nitrogen atom. The fragmentation peaks due to the fission of sulfur–carbon



SCHEME 3 Mass fragmentations of sulfonediimine (**3**).

linkage were also clearly observed though they gave small peaks. The fragmentation of **3** is shown in Scheme 3.

EXPERIMENTAL

General. Melting points of the products were measured by a Yanaco instrument and are uncorrected. IR spectra were obtained using a Hitachi 215 spectrometer. ^{1}H NMR spectra of all the compounds were obtained with a Hitachi Perkin-Elmer R-20 spectrometer in 20% solutions in $CDCl_3$ using TMS as an internal standard. Mass spectrum were recorded on a Hitachi RMU-6MG mass spectrometer with a direct inlet system. Elemental analyses were carried out at the Chemical Analysis Center of this University. Oxidizing agents, *m*-chloroperbenzoic acid, 5% aqueous sodium hypochlorite solution, and Chloramine-*T* were obtained from Wako Pure Chemicals. The latter one was dehydrated by the method reported earlier.[23] *O*-Mesitylenesulfonylhydroxylamine (MSH) was prepared by the method[24] reported previously. Anhydrous acetonitrile was purified by the usual procedures.[25] Other chemicals were of reagent grade.

Preparation of diphenylsulfoximine (**1a**). In a typical run, to a methanol solution (2 ml) of **1a** (1.0 g, 4.6 mmol), 5% aqueous hypochlorite solution (7.0 g) was added and the mixture was kept stirring for 24 h at 25°C. Then, the mixture was poured into water (50 ml) and the aqueous solution was extracted with chloroform. The extract was washed with aqueous HCl (6N, 30 ml), the water layer was separated, made alkaline with aq. NaOH solution (40 ml) again extracted with chloroform, and then the chloroform extract was dried ($MgSO_4$). After the solvent was removed *in vacuo*, the sulfoximine was obtained as a white precipitate which was then recrystallized from benzene. Yield 0.99 g (100%). mp 103°C. Similarly, other *N*-unsubstituted sulfoximines (**1**) were prepared and listed in Table I.

Preparation of diphenylsulfiliminodiphenylsulfonium perchlorate. To a solution of *tert*-butyl hypochlorite (1.2 g, 10.8 mmol)[26] in dry dichloromethane (15 ml) at −70°C a solution of diphenyl sulfide (2.0 g, 10.8 mmol) in dry dichloromethane (10 ml) was added slowly. The mixture was stirred at this temperature for 10 min followed by slow addition of dry NH_3 gas (ca. 20–30 ml as liq. NH_3). The temperature was allowed to rise to −50°C and the reaction mixture was stirred for 3 h at that temperature. Then, the mixture was washed with aq. sodium perchlorate solution at room temperature and with water three times. The organic layer was dried ($MgSO_4$), concentrated *in vacuo*. The sulfonium perchlorate was obtained in 98% yield. Recrystallization from chloroform–pentane. mp 172.0–172.5°C (lit. 172–172.5°C).[20]

Reaction of phenyl-p-tolyl-tert-butoxysulfonium chloride with diphenylsulfilimine in liq. NH_3. To a solution of **4a** (402 mg, 2.0 mmol) in liq. NH_3 at −50°C, a solution of phenyl-*p*-tolyl-*tert*-butoxysulfonium chloride generated *in situ* from the reaction of phenyl *p*-tolyl sulfide (400 mg, 2.0 mmol) with *tert*-butyl hypochlorite (220 mg, 2.0 mmol) in dichloromethane was added slowly. The reaction mixture was stirred for 3 h at this temperature and was allowed to come up to room temperature. After the usual work-up processes, diphenylsulfilimino-*p*-tolylphenylsulfonium perchlorate was obtained in 96% yield.

Reaction of diphenylsulfilimine with Chloramine-T in MeOH. To the methanol solution of **4a** (200 mg, 0.91 mmol), was added Chloramine-*T* (400 mg, 1.4 mmol) in 2 ml of methanol and the mixture was heated for 4 h at 40°C. Methanol was evaporated and the residual oil was poured onto 10 ml of 10% NaOH solution. The aqueous solution was extracted with chloroform. The chloroform solution was shaken with aq. 6*N*-HCl twice to separate the sulfoximine. The chloroform solution was made alkaline and washed twice with water, dried over ($MgSO_4$). The solvent was removed under reduced pressure to afford colorless precipitate which was recrystallized from ethanol affording **2a** (101 mg) in 30% yield. mp 153.0–153.5°C. When the acid solution was made alkaline, **1a** (79 mg) was obtained in 40% yield. mp 103.0°C.

Preparation of diphenyl-N-tosyl-sulfonediimine (**2a**). Typically, **4a** (5.0 g, 25 mmol) and 5 molar excess of TsNHNa were dissolved in 300 ml of anhydrous acetonitrile at 40°C. To this solution, 10.0 g of anhydrous Chloramine-*T* was added. The mixture was stirred for 24 h at 40°C. After the solvent was removed, the residue was suspended in 10% aqueous NaOH solution. The aqueous solution was extracted with chloroform. After chloroform was evaporated, the residue was recrystallized from ethanol. **2a** (8.3 g) was obtained in 90% yield. mp 153.0–153.5°C. Similarly, several sulfonediimines (**2**) were prepared and the results are summarized in Table II.

Preparation of diphenylsulfonediimine (**3a**). **2a** (1.0 g, 5 mmol) was dissolved in 5 ml of conc. H_2SO_4 (97%), stirred for 48 h at 35°C, and then poured onto ice-water. The aqueous solution was made alkaline with 50% aq. NaOH solution and extracted with chloroform. After the solvent was removed, the residue

was recrystallized from diethyl ether, and **3a** was obtained quantitatively. mp 91–92°C. Other sulfonediimines (**3**) were obtained similarly and the results are summarized in Table III.

Isolation of diphenyl-N-chlorosulfilimine (**5a**) *during preparation of N-tosyl-sulfonediimine.* When 5 min passed after starting the reaction of **3a** (500 mg, 2.5 mmol) with Chloramine-*T* (620 mg, 2.7 mmol) and TsNHNa (4.8 g, 25 mmol), the reaction mixture was poured into ice-water to stop the reaction. After the usual work-up, **5a** (410 mg) was obtained in 70% yield.

Reaction of **5a** *with NaOH in aqueous methanol.* **5a** (400 mg, 1.7 mmol) was dissolved in aqueous acetonitrile (2 ml), cooled to 0°C. To an aqueous methanol solution (60%, 10 ml) of NaOH (680 mg, 17.0 mmol), the acetonitrile solution of **5a** was added dropwise under cooling at 0°C, and the reaction mixture was stirred at 20°C until **5a** disappeared by TLC. The resulting mixture was extracted with chloroform and then the chloroform solution was extracted with 6N-HCl. The aqueous solution was neutralized with aqueous NaOH and again extracted with chloroform, dried ($MgSO_4$). The solvent was removed *in vacuo*, and **1a** (350 mg) was obtained in 95% yield.

Reaction of **5a** *with TsNHNa in anhydrous acetonitrile.* **5a** (500 mg, 2.1 mmol) was dissolved in anhydrous acetonitrile (5 ml), cooled at 0°C. To an excess of TsNHNa (4.1 g, 21 mmol) in anhydrous acetonitrile (50 ml) was added the solution of **5a** at 20°C and the solution was heated to 40°C with stirring until **5a** disappeared. After usual work-up, **2a** (550 mg) was obtained in 70% yield.

Reaction of **5a** *with liq.* NH_3. **5a** (500 mg, 2.1 mmol) was dissolved in acetonitrile (10 ml), cooled to -50°C and NH_3 was introduced. The reaction was continued at -50°C for 24 h. After removing NH_3 and acetonitrile, a viscous product was purified by column chromatography using chloroform as an eluent. **3a** was obtained, 261 mg (57%). mp 91–91.5°C.

Reaction of **5a** *with propylamine.* **5a** (500 mg, 2.1 mmol) was dissolved in acetonitrile (5 ml), treated with propylamine at 25°C, and stirred at 25°C for 24 h. Similar work-up process as described above, diphenyl-*N*-propylsulfonediimine (296 mg) was obtained in 54% yield, mp 117.5–118.5 °C (CH_2Cl_2–pentane recrystallization). Calcd. for $C_{15}H_{18}N_2S$: C, 69.72; H, 7.02; N, 10.84%. Found: C, 69.72; H, 7.01; N, 10.85%. IR (KBr): 3160 (NH), 1170, 1110, 1035, and 1010 (NSN). ^{1}H NMR ($CDCl_3$, TMS) 0.95 (3 H, t, $-NCH_2CH_2C\underline{H}_3$), 1.62 (2 H, sept, $-NCH_2C\underline{H}_2CH_3$) 1.88 (1 H, s, NH), 2.97 (2H, t, $-NC\underline{H}_2CH_2CH_3$) and 7.23–8.05 (10 H, m, aromatic protons).

Diphenyl-*N*-butylsulfonediimine was prepared similarly. Yield 43%; mp 97.5–98.0°C. Calcd. for $C_{16}H_{20}N_2S$: C, 70.54; H, 7.40; N, 10.28%. Found: C, 70.37; H, 7.42; N, 10.19%. IR (KBr) 3160 (NH), 1180, 1085, 1060, 1025, 985 (NSN). ^{1}H NMR ($CDCl_3$, TMS) 0.87 (3 H, t, $-N(CH_2)_3C\underline{H}_3$), 1.27 (2 H, m, $-N(CH_2)_2C\underline{H}_2CH_3$), 1.53 (2 H, m, $-NCH_2C\underline{H}_2CH_2CH_3$), 1.72 (1 H, s, NH), 2.95 (2 H, t, $-NCH_2(CH_2)_2CH_3$), 7.17–8.63 (10 H, m, aromatic protons).

Caution. The *N*-chlorosulfilimine is extremely sensitive to shock and light. An attempt to dry a sample of ca. 3.0 g of diphenyl-*N*-chlorosulfilimine resulted in violent decomposition, breaking the drying apparatus. Another example of the explosion is the following: after a purified sample of ca. 1 g of the *N*-chlorosulfilimine was stored in a refrigerator at -20°C for 24 h and then warmed to room temperature, it decomposed violently after contacting with air. Thus, it is recommended that the *N*-chlorosulfilimine is dried only behind a safety shield, and should be protected from direct irradiation of light, and should be used immediately after purification, not stored even in a refrigerator.

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