

Preparation of *S,S*-Diphenylsulfilimines, -sulfoximines, and -*N*-(*p*-tolylsulfonyl)sulfonediimines *N*-Substituted with Sulfur Groups of Different Oxidation States

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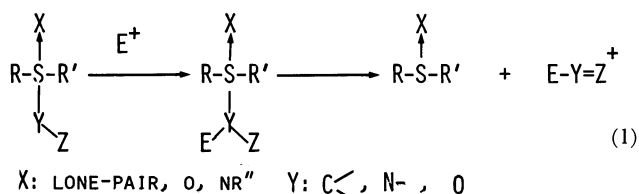
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S,S-Diphenyl-*N*-(*p*-tolylthio)-, -*N*-(*p*-tolylsulfinyl)-, -*N*-(*p*-toluenesulfinimidoyl)-, -*N*-(*p*-tolylsulfonyl)-, and -*N*-(*p*-toluenesulfonylimidoyl)sulfoximines have been synthesized either by sulfonylation, sulfinylation, sulfinimidoylation, sulfonylation, and sulfonylimidoylation or by oxidation of the *N*-substituted sulfoximines with sulfur groups of lower oxidation states, *i.e.*, the *N*-sulfonylated sulfoximine. Similar attempts have been made on similarly substituted sulfonediimines. Sulfonylation and sulfonylation of *N*-unsubstituted *N*-(*p*-tolylsulfonyl)sulfonediimine were unsuccessful but its sulfinylation underwent nicely. An attempt to disulfonylation of the *N,N'*-unsubstituted sulfonediimine ended up in the monosulfonylation. *N,N'*-bis(*p*-Tolylsulfonyl)sulfonediimine was successfully prepared by oxidation of the *N*-(*p*-tolylsulfinyl)-*N'*-(*p*-tolylsulfonyl)sulfonediimine with *m*-chloroperbenzoic acid.

Numerous *N*-substituted sulfilimines,¹⁾ sulfoximines,²⁾ and *N'*-*p*-tolylsulfonylsulfonediimines,³⁾ such as *N*-alkyl-, *N*-aryl-, *N*-sulfonyl-, *N*-acyl-, *N*-silyl-, and *N*-phosphoryl derivatives, have been prepared. In general, these compounds are fairly stable. Whereas, only a few *N*-substituted derivatives having a heteroatom with lone-pair electrons directly attached to the imino nitrogen atom of sulfilimine have been known. Furthermore, very little of the chemistry of these compounds has been explored. The compounds actually isolated are *N*-chloro-,⁴⁾ *N*-bromo-,⁴⁾ *N*-iodo-,⁴⁾ *N*-sulfonyl-,⁵⁾ *N,N*-phthaloyl-,⁶⁾ *N*-aryl-⁷⁾ derivatives which are in general thermally unstable as compared to other *N*-substituted derivatives having an atom with no electron pair in the *N*-substituent directly combined to the imino nitrogen atom. These sulfilimines bearing *N*-substituents of heteroatoms possessing lone-pair electrons, are generally quite reactive and readily decompose *via* the initial S–N bond fission. These reactive derivatives, upon activation by addition of a suitable electrophile such as sulfonyl chloride, undergo facile cleavage of the S–N linkage. For example, the *N*-chlorosulfilimine readily decomposes even at room temperature to afford the corresponding sul-

fide and the sulfonium salt ($\text{Ph}-\text{S}(\text{Ph})=\text{N}^+-\text{S}(\text{Ph})_2 \text{Cl}^-$) and the decomposition is accelerated further by addition of Brönsted acids. The structures of these activated derivatives formed by addition of an electrophile are considered to be analogous to that of the persulfoxide,⁸⁾ or that of the intermediates formed in the treatment of dimethyl sulfoxide with primary or secondary alcohols to afford aldehydes or ketones,⁹⁾ or those of the reactions of sulfoxides,¹⁰⁾ sulfilimines,¹¹⁾ sulfonium ylides,¹²⁾ and sulfoximines¹³⁾ with carbenes or nitrenes, to afford eventually the reduction products (Eq. 1).



The repulsive interaction between lone-pair electrons of the imino nitrogen and the adjacent heteroatom is considered to weaken the S–N linkage for facile cleavage. Meanwhile, the sulfilimines having either *N*-aryl-, or *N*-phthalimido-substituent attached to the imino nitrogen are relatively stable thermally because the repulsive interactions of lone-pair electrons between the nitrogen atom and the adjacent sulfur atom is relieved considerably in these compounds. Similarly, the *N*-chlorosulfoximine, in which the repulsive interaction between two adjacent heteroatoms is reduced, undergoes degradation to afford the corresponding sulfoxide only at an elevated temperature, *e.g.*, 200 °C.

In order to explore the rough correlation between the nature of the S–N linkage and the stability of the sulfilimine derivatives, various *S,S*-diaryl-*N*-substituted sulfilimines (1), -*N*-substituted sulfoximines (2), and *N,N'*-substituted-*N*-(*p*-tolylsulfonyl)sulfonediimines (3) containing an S–N group, *e.g.*, *N*-(*p*-tolylthio)-, *N*-(*p*-tolylsulfinyl)-, *N*-(*p*-toluenesulfinimidoyl)-, and *N*-(diphenylsulfonyl)sulfonium derivatives have been synthesized and their chemical properties have been examined.

Definition of Abbreviation for the Compounds.

The following numbering and abbreviation for the *S,S*-diphenyl sulfur compounds are used through this paper.

$\text{Ph}-\text{S}-\text{Ph} : \text{N}-\text{R}-\text{Substituted-}S,S\text{-diphenylsulfilimines}$
 $\downarrow$
 NR (1),

$\text{Ph}-\text{S}-\text{Ph} : \text{N}-\text{R}-\text{Substituted-}S,S\text{-diphenylsulfoximines}$
 $\swarrow \searrow$
 O NR (2),

$\text{Ph}-\text{S}-\text{Ph} : \text{N},\text{N}'-\text{R},\text{R}'\text{-Disubstituted-}S,S\text{-diphenylsul-}$
 $\swarrow \searrow$
 RN NR' fonediiimines (3),

R or R' groups:

R (or R'); H, *N*-unsubstituted- (a),
 ; -STol(*p*-), *N*-(*p*-tolylthio)- (b),
 ; -S(O)Tol(*p*-), *N*-(*p*-tolylsulfinyl)- (c),

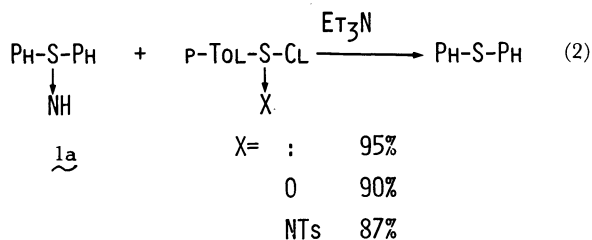
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- ; -S(NTs)Tol(*p*-), *N*-(*p*-toluenesulfinimidoyl)- (d),
- ; -S(O)₂Tol(*p*-), *N*-(*p*-tolylsulfonyl)- (e),
- ; -S(O)(*p*-TolN)Ph, *N*-(*p*-toluenesulfonylimidoyl)- (f),
- ; -S(Ph)₂, *N*-(diphenylsulfo)- (g).

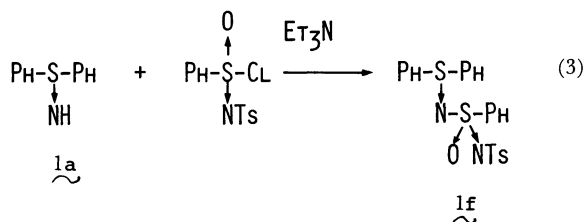
other derivatives are shown by their *N*-substituent and numbering of the compounds *e.g.*, *N*-chloro-(1). Therefore, for example, **1b** and **3ab** indicate *N*-(*p*-tolylthio)-S,S-diphenylsulfilimine and *N'*-unsubstituted *N*-(*p*-tolylthio)-S,S-diphenylsulfonediimine respectively.

Results and Discussion

***N*-Substituted S,S-Diphenylsulfilimines (1).** Treatment of *N*-unsubstituted sulfilimines with *p*-toluenesulfonyl chloride gave the corresponding thermally extremely stable compounds, *N*-(*p*-tolylsulfonyl)-sulfilimines. However, *N*-(*p*-tolylthio)-(**1b**), *N*-(*p*-tolylsulfonyl)-(**1c**), *N*-(*p*-toluenesulfinimidoyl)-(**1d**), or *N*-(*p*-toluenesulfonylimidoyl)sulfilimines (**1f**) have not been reported in the literature. Preparations of **1b**—**d** have been attempted, by treating *N*-unsubstituted sulfilimine (**1a**) with *p*-toluenesulfonyl chloride, *p*-toluenesulfinyl chloride, or *p*-toluenesulfinimidoyl chloride in the presence of triethylamine, however only the corresponding reduction product, the sulfide, was obtained (Eq. 2).

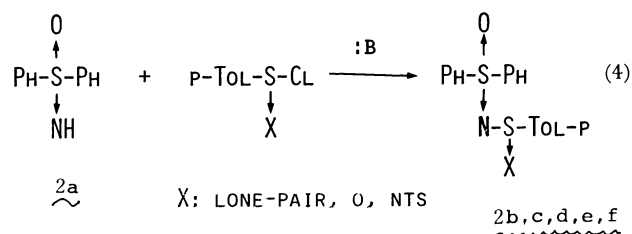


Finally, diphenyl *N*-(benzenesulfonylimidoyl)sulfilimine (**1f**) was prepared by treating **1a** with *N*-benzenesulfonylimidoyl chloride in the presence of triethylamine in 89% yield.

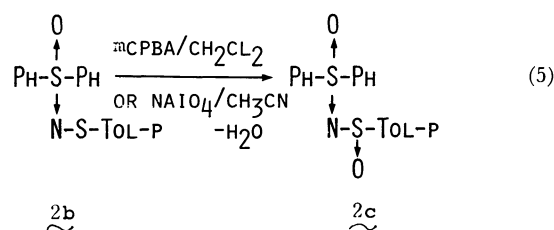


***N*-Substituted S,S-Diphenylsulfoximines (2).** Conversion of *N*-unsubstituted sulfoximines into the corresponding *N*-(*p*-tolylsulfonyl)sulfoximines and the desulfonylation of the latter compound are well known. Thus, *N*-unsubstituted S,S-diphenylsulfoximine (**2a**) was shown to react with *p*-toluenesulfonyl chloride in pyridine affording quantitatively the corresponding **2e**, which can reproduce **2a** by treating with concentrated sulfuric acid¹⁴ or sodium in liquid ammonia.¹⁵ However, nothing is known about *N*-substituted sulfoximines (**2b**, **2c**, **2d**, and **2f**). In the course of our systematic study of sulfilimines and their derivatives, especially the bonding nature of the semipolar S-N linkage in sulfilimines, sulfoximines

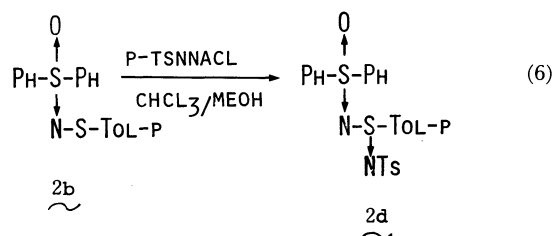
and sulfonediimines, these compounds have been prepared in order to compare the characteristic properties of these bonds with those of known *N*-unsubstituted sulfoximines or *N*-(*p*-tolylsulfonyl)sulfoximines. **2b** was prepared by treating *N*-sodium salt of the sulfoximine with *p*-toluenesulfonyl chloride or by treatment of two equivalents of **2a** with *p*-toluenesulfonyl chloride. Other bases such as pyridine or triethylamine gave no good result. The sulfoximines, **2c**, **2d**, and **2f** were prepared by treating the *N*-sodium salt of the sulfoximine with *p*-toluenesulfinyl chloride, *p*-toluenesulfinimidoyl chloride, and *p*-toluenesulfonylimidoyl chloride, respectively, in good yields. These compounds were able to be prepared using other bases such as pyridine or triethylamine in good yields.



Another route to prepare **2c**, **2d**, and **2f** has been examined, using **2b** as the key starting material, which was converted to other *N*-substituted **2** by oxidation with such oxidizing reagents, as *m*-chloroperbenzoic acid (**mCPBA**) and sodium salt of *N*-chloro-*p*-toluenesulfonamide (chloramine-*T*). **2b** was oxidized readily with one equivalent of sodium periodate in aqueous acetonitrile or **mCPBA** in dichloromethane to **2c** (Eq. 5).

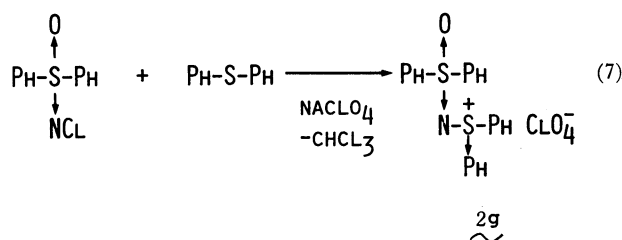


Meanwhile, **2b** reacts with chloramine-*T* to afford **2d** in a good yield in chloroform-methanol solution (Eq. 6).



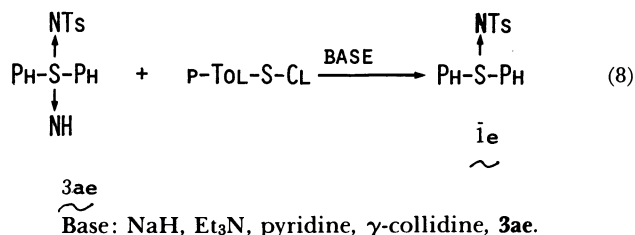
The use of two-fold excess of **mCPBA** in dichloromethane converted **2a** to **2e**, while the use of one equivalent of **mCPBA** oxidized **2c** to **2e**. Thus, these oxidation reactions of **2b** or **2c** should be another convenient way to prepare **2e**. In the same way, **2d** was nicely converted to **2f** by treating with **mCPBA** in dichloromethane in a good yield. Thus, **2b** is a good starting material for preparation of various other *N*-substituted sulfoximine derivatives. **2g** was also prepared by the

reaction of the *N*-chloro-2 with the sulfide, according to the method reported earlier¹⁰⁾ (Eq. 7).



Thus, one can prepare all kinds of *N*-substituted sulfoximines, **2b–g**. The results are summarized in Scheme 1 and Tables 1 and 2.

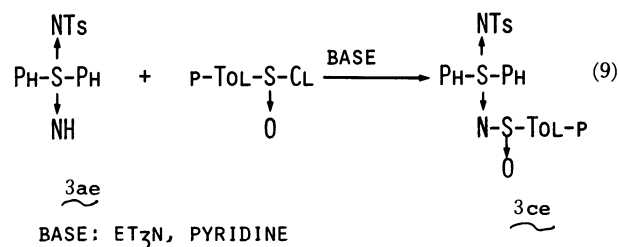
Preparation of *N'*-Substituted *S,S*-Diphenyl-*N*-(*p*-tolylsulfonyl)sulfonediimines (3**).** Treatment of *N'*-unsubstituted *S,S*-diphenyl-*N*-(*p*-tolylsulfonyl)sulfonediimines (**3ae**) with *p*-toluenesulfonyl chloride at -20°C in the presence of bases, *e.g.*, pyridine, triethylamine or **3ae**, did not afford the corresponding **3be** at all, but the reduction product, **1e** was obtained in a high yield (Eq. 8).

TABLE 1. PREPARATION OF *N*-SUBSTITUTED-SULFOXIMINES

$\begin{array}{c} \text{O} \\ \uparrow \\ \text{Ph-S-Ph} \\ \downarrow \\ \text{N-X} \\ \text{X} \end{array}$	Condition	Yield/% ^{a)}
S-Tol- <i>p</i> (b)	<i>p</i> -TolS(NTs)Cl, NaH/PhH	92
	<i>p</i> -TolS(NTs)Cl, $\begin{array}{c} \text{O} \\ \uparrow \\ \text{Ph-S-Ph} \\ \downarrow \\ \text{NH} \end{array}$ /Et ₂ O	81
S-C ₆ H ₄ -NO ₂ - <i>o</i>	<i>p</i> -TolS(NTs)Cl, py/Et ₂ O	8
	<i>p</i> -TolS(NTs)Cl, Et ₃ N/Et ₂ O	10
	<i>o</i> -NO ₂ C ₆ H ₄ S(NTs)Cl, NaH/PhH	98
	<i>o</i> -NO ₂ C ₆ H ₄ S(NTs)Cl, $\begin{array}{c} \text{O} \\ \uparrow \\ \text{Ph-S-Ph} \\ \downarrow \\ \text{NH} \end{array}$ /Et ₂ O	95
	<i>p</i> -TolS(NTs)Cl, NaH/PhH	95
S-Tol- <i>p</i> (c)	<i>p</i> -TolS(NTs)Cl, NaH/PhH	92
	<i>p</i> -TolS(NTs)Cl, Et ₃ N/Et ₂ O	92
	<i>p</i> -TolS(NTs)Cl, py/Et ₂ O	90
	<i>m</i> CPBA/CH ₂ Cl ₂ , $\begin{array}{c} \text{O} \\ \uparrow \\ \text{Ph-S-Ph} \\ \downarrow \\ \text{NH} \end{array}$	85
	<i>m</i> CPBA/CH ₂ Cl ₂ , $\begin{array}{c} \text{O} \\ \uparrow \\ \text{Ph-S-Ph} \\ \downarrow \\ \text{N-S-Tol-}p \end{array}$	95

a) Isolated yield.

However, the reaction of **3ae** with *p*-toluenesulfonyl chloride at -20°C in the presence of bases, *e.g.*, pyridine or triethylamine proceeded nicely (Eq. 9)

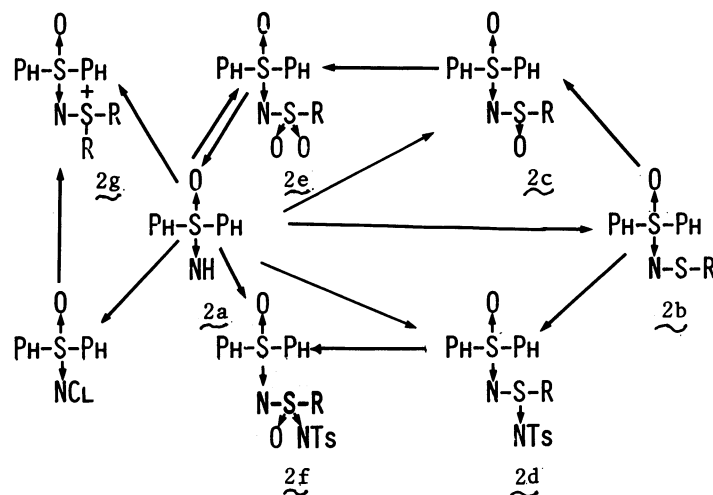


Furthermore, treatment of **3aa** with an equimolar amount of *p*-toluenesulfonyl chloride gave only **3ae**, monosulfonylated product. Disulfonylation of **3aa** was attempted by treating **3ae** with *p*-toluenesulfonyl chloride under various conditions and failed, recovering only **3ae** quantitatively. However, interestingly, **3ce**, *N,N'*-bis(*p*-tolylsulfonyl)sulfonediimine, was obtained in a quantitative yield when **3ce** was oxidized with 1 equiv of *m*CPBA (Eq. 10).

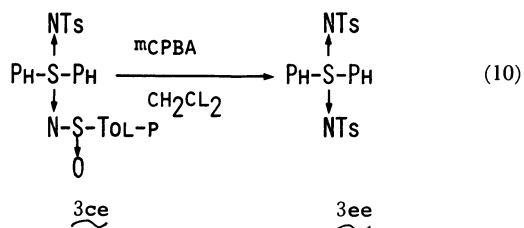
TABLE 2. PREPARATION OF *N*-SUBSTITUTED-SULFOXIMINES (2)

X	Condition	Yield/% ^{a)}
S-Tol- <i>p</i> (c)	NaIO ₄ /70% CH ₃ CN, $\begin{array}{c} \text{O} \\ \uparrow \\ \text{Ph-S-Ph} \\ \downarrow \\ \text{N-S-Tol-}p \end{array}$	96
	<i>p</i> -TolS(NTs)Cl, NaH/PhH	75
S-Tol- <i>p</i> (d)	<i>p</i> -TsNNaCl/CHCl ₃ /MeOH, $\begin{array}{c} \text{O} \\ \uparrow \\ \text{Ph-S-Ph} \\ \downarrow \\ \text{N-S-Tol-}p \end{array}$	87
	<i>p</i> -TsNNaCl/CH ₃ CN, $\begin{array}{c} \text{O} \\ \uparrow \\ \text{Ph-S-Ph} \\ \downarrow \\ \text{N-S-Tol-}p \end{array}$	90
OClO ₃ ⁻ + S-Ph Ph (g)	PhSPh, PhSPh, NaOClO ₃ /CHCl ₃ , $\begin{array}{c} \text{O} \\ \uparrow \\ \text{Ph-S-Ph} \\ \downarrow \\ \text{N-S-Tol-}p \end{array}$	80
	(2 equiv) <i>m</i> CPBA/CH ₂ Cl ₂ , $\begin{array}{c} \text{O} \\ \uparrow \\ \text{Ph-S-Ph} \\ \downarrow \\ \text{N-S-Tol-}p \end{array}$	99
S-Tol- <i>p</i> (f)	<i>m</i> CPBA/CH ₂ Cl ₂ , $\begin{array}{c} \text{O} \\ \uparrow \\ \text{Ph-S-Ph} \\ \downarrow \\ \text{N-S-Tol-}p \end{array}$	95
	<i>p</i> -TolS(NTs)Cl, NaH/PhH, $\begin{array}{c} \text{O} \\ \uparrow \\ \text{Ph-S-Ph} \\ \downarrow \\ \text{N-S-Tol-}p \end{array}$	53
S-Tol- <i>p</i> (f)	<i>m</i> CPBA/CH ₂ Cl ₂ , $\begin{array}{c} \text{O} \\ \uparrow \\ \text{Ph-S-Ph} \\ \downarrow \\ \text{N-S-Tol-}p \end{array}$	79
	<i>m</i> CPBA/CH ₂ Cl ₂ , $\begin{array}{c} \text{O} \\ \uparrow \\ \text{Ph-S-Ph} \\ \downarrow \\ \text{N-S-Tol-}p \end{array}$	79

a) Isolated yield.



Scheme 1. Diagram of *N*-substituted sulfoximine starting from unsubstituted sulfoximine.



The lack of reactivity of **3ae** toward the sulfonyl chloride and the facile reaction of **3ce** with **mCPBA** may be

TABLE 3. PREPARATION OF *N*-SUBSTITUTED-*N'*-*p*-TOLUENESULFONYLSULFONEDIIMINES (**3**)

$\begin{array}{c} \text{NTs} \\ \uparrow \\ \text{Ph}-\text{S}-\text{Ph} \\ \downarrow \\ \text{N}-\text{X} \\ \text{(3)} \\ \text{X} \end{array}$	Condition	Yield/% ^a
S-Tol- <i>p</i>	<i>p</i> -TolSCL, NaH/PhH	0
(b)	$\begin{array}{c} \text{NTs} \\ \uparrow \\ \text{Ph}-\text{S}-\text{Ph} \\ \downarrow \\ \text{NH} \end{array}$	0
	<i>p</i> -TolSCL, Ph-S-Ph/CH ₂ Cl ₂	0
	<i>p</i> -TolSCL, py/CH ₂ Cl ₂	0
	<i>p</i> -TolSCL, γ -collidine/CH ₂ Cl ₂	0
S-Tol- <i>p</i>	<i>p</i> -TolSCL, Et ₃ N/CH ₂ Cl ₂	0
	<i>p</i> -TolS(O)Cl, Et ₃ N/CH ₂ Cl ₂	85
	<i>p</i> -TolS(O)Cl, py/CH ₂ Cl ₂	80
(c)		
O S-Tol- <i>p</i> O	<i>p</i> -TolSO ₂ Cl, NaH/PhH	0
	<i>p</i> -TolSO ₂ Cl, Et ₃ N/CH ₂ Cl ₂	0
	<i>p</i> -TolSO ₂ Cl, py/CH ₂ Cl ₂	0
	<i>p</i> -TolSO ₂ Cl, γ -collidine/CH ₂ Cl ₂	0
	$\begin{array}{c} \text{NTs} \\ \uparrow \\ \text{Ph}-\text{S}-\text{Ph} \\ \downarrow \\ \text{N}-\text{S}-\text{Tol-}p \\ \downarrow \\ \text{O} \end{array}$	94

a) Isolated yield.

reasonably rationalized in the following manner.

Namely, in the former reaction, the nucleophilicity of the imino nitrogen of **3ae** is considerably diminished while the sterically bulky sulfonyl group attached to the imino group would hinder the second sulfonylation of the imino nitrogen; whereas in the latter reaction, no matter whether the oxidation is caused by electrophilic attack of **mCPBA** or nucleophilic attack of the perbenzoate anion, the approach of the oxygen atom of **mCPBA** toward the sulfinyl sulfur atom should not be hindered both sterically and electronically.

These new derivatives of sulfonediimines thus obtained were identified by both spectroscopic and elemental analyses. This is the first and perhaps the best method to prepare *S,S*-diaryl-*N,N'*-bis(*p*-tolylsulfonyl)sulfonediimine. These results are listed in Table 3.

Experimental

General. Melting points of the products were measured by Yanaco instrument and were uncorrected. IR spectra were obtained using a Hitachi 215 spectrophotometer. ¹H NMR spectra of the all compounds were obtained with a Hitachi Perkin-Elmer R-20 spectrometer in 20% solutions in deuteriochloroform using tetramethylsilane as an internal standard. Mass spectra were recorded on a Hitachi RMU-6MG mass spectrometer with a direct inlet system. Liquid chromatographs were obtained by Yanaco L-1030 instrument using methanol as an eluent. Thin-layer chromatographies were carried out with Merck DC-Plastikofolien Kieselgel 60 F 254 Art 5735 with fluorescent indicator using various solvents and mixed solvents. Development was followed by UV light or by coloring with iodine. Silica gel used for column chromatography was either of Wako or of Merck chromatographic grade. Elemental analyses were carried out at the Chemical Analysis Center of this University. Oxidizing agents, **mCPBA**, sodium periodate and chloramine-*T* were obtained from Wako Pure Chemicals. Anhydrous dichloromethane and ether were obtained by the usual procedures.¹⁷ Other chemicals were of reagent grade.

***p*-Toluenesulfonyl Chloride.** *p*-Toluenesulfonyl chloride was prepared by treating the corresponding disulfide with gaseous chlorine in dichloromethane at 5°C, accord-

ing to the known method,^{18,19} and purified by distillation under reduced pressure. Bp 76.0–78.0 °C/2.5 mmHg (1 mmHg ≈ 133.322 Pa),¹⁸ (77.5–78.2 °C/2.5 mmHg).

***o*-Nitrobenzenesulfinyl Chloride.** Mp 74.0–75.0 °C (from tetrachloromethane), (lit, 75 °C¹⁹).

***p*-Toluenesulfinyl Chloride.** *p*-Toluenesulfinyl chloride was obtained by treatment of *p*-toluenethiol with gaseous chlorine in anhydrous acetic anhydride at 10 °C, in the usual manner.²⁰ Bp 107.0–109.5 °C/2.5 mmHg, (lit, 92–102 °C/0.5 mmHg).²⁰

***p*-Toluenesulfinimidoyl Chloride.** *p*-Toluenesulfinimidoyl chloride was prepared by the reaction of *p*-toluenesulfinyl chloride with anhydrous chloramine-*T* in benzene, according to the previously reported method.²¹ Mp 141.5–142.5 °C, (lit, 141.5–142.5 °C).²¹

***N*-(*p*-Tolylsulfonyl)-*p*-toluenesulfinimidoyl Chloride.** *p*-Toluenesulfinimidoyl chloride was prepared by the reaction of *p*-toluenesulfinyl chloride with commercially available chloramine-*T* in benzene, according to the method reported earlier.²² Mp 76.5–77.5 °C, (lit, 76–78 °C).²²

Preparation of 1a, 2a, 3ae. 1a,²³ 2a,²⁴ and 3ae²⁵ were prepared by the method reported earlier.

Preparation of 1a, 2a, 3ae. 1a,²³ 2a,²⁴ and 3ae²⁵ were prepared by the method reported earlier.

Preparation of *N*-Chlorosulfoximine. 3a (2.0 g, 9.2 mmol) was dissolved in 10 mL of acetonitrile. This solution was added to a stirred solution of 15 mL of cold sodium hypochlorite solution. The reaction mixture was stirred for 15 min before the starting sulfoximine disappeared upon checking the TLC or HPLC. The solution was extracted with chloroform, which was dried, filtrated and evaporated. The purification was performed on recrystallization from benzene. Yield was 1.85 g (80%), colorless crystals, mp 150.0–151.0 °C.

Preparation of 1f. To a mixture of 1a (200 mg, 0.91 mmol) and triethylamine (138 mg) in chloroform, a chloroform solution of *N*-(*p*-tolylsulfonyl)benzenesulfinimidoyl chloride (300 mg, 0.91 mmol) was added. After stirring the reaction mixture for 30 min at 25 °C, solid precipitates were washed with dilute aqueous hydrochloric acid solution, water, and dried over magnesium sulfate. After the solvent was removed, the crude product was purified by column chromatography. The crystals were recrystallized from ethanol. Yield was 401 mg (89%), mp 139.5 °C; IR (KBr) 1315(SO₂), 1305(SO₂), 1240(O=S–N–), 1150(SO₂), 1100(O=S–N–), 1060(O=S–N–), 1035, 1021, and 995 cm^{–1}; ¹H NMR (CDCl₃) δ=2.32 (3H, s, –SO₂C₆H₄CH₃–*p*), 7.00–7.90 (19H, m, aromatic protons); MS (20 eV) *m/z* (rel intensity) (M⁺; 0.3), 292(7), 248(36), 186([PhSPh]⁺; 100), 171(84), 170(81), 155(5), 125(11), 109(13), 90(23), and 77(18). Found: C, 60.70; H, 4.27; N, 5.50%. Calcd for C₂₅H₂₂N₂O₃S₃: C, 60.70; H, 4.48; N, 5.66%.

Preparation of 2b. To the ethereal solution of 2a (10 g, 46 mmol) was added *p*-toluenesulfinyl chloride (3.5 g, 22 mmol) in ether solution under cooling with a Dry Ice–acetone bath with stirring. The reaction mixture was kept at –70 °C for 10 min and the cooling bath was removed and the heterogeneous reaction mixture was stirred until the solution reached at room temperature. The precipitates formed were filtered off after stirring the solution at 25 °C for 20 min. The solvent was evaporated. The crude product was purified through column chromatography and crystals thus obtained were recrystallized from dichloromethane–pentane. Yield was 6.1 g, 81%, mp 110 °C. Sodium salt of *S,S*-diphenylsulfoximine, which was prepared from 2a and sodium hydride in benzene, also afforded 2b by the reaction with *p*-toluenesulfinyl chloride in 92% yield. Colorless crystals; mp 110 °C; IR (KBr) 1220(O=S–N–), 1085(O=S–N–), and 980(O=S–N–); ¹H NMR (CDCl₃) δ=2.26 (3H, s, –C₆H₄CH₃–

p), 6.96–8.09 (14H, m, aromatic protons); MS (20 eV) *m/z* (rel intensity) 339(M⁺; 7), 246(50), 202([PhS(O)Ph]⁺; 100), 186(75), 174(22), 154(77), 136(22), 123(61), 97(31), 90(31), and 77(17). Found: C, 67.11; H, 4.86; N, 4.15%. Calcd for C₁₉H₁₇NOS₂: C, 67.22; H, 5.04; N, 4.12%.

Preparation of *S,S*-Diphenyl-*N*-(*o*-nitrophenylthio)sulfoximine. Yield was 95–98%; colorless crystals; mp 161.0–162.0 °C; IR (KBr) 1210 (O=S–N–), 1090 (O=S–N–), 1005, and 985 (–S–N–); ¹H NMR (CDCl₃) δ=6.87–8.17 (14H, m, aromatic protons); Found: C, 58.29; H, 3.81; N, 7.45%. Calcd for C₁₈H₁₄N₂O₃S₂: C, 58.36; H, 3.80; N, 7.56%.

Preparation of 2c. This compound was prepared by either one of the following two processes.

Method A: 2a (3.0 g, 13.8 mmol) and triethylamine (1.7 g, 16.6 mmol) were dissolved in ether. Under stirring and cooling with a Dry Ice–acetone bath, and ethereal solution of *p*-toluenesulfinyl chloride (2.5 g, 14.3 mmol) was added dropwise. After warming at 25 °C for 20 min the precipitates were separated by filtration. Ether was removed, the crude crystals thus obtained were recrystallized from dichloromethane–pentane. Yield was 4.5 g, 92%; mp 192.5–193.0 °C; colorless crystals.

Method B: 2b (300 mg, 0.88 mmol) was oxidized with mCPBA (152 mg) at 25 °C for 15 min. The usual work-up process afforded 2c. Yield was 267 mg, 85%; IR (KBr) 1235(O=S–N–), 1105(O=S–N–), 1090(O=S–N–), 1075(–S=O), 1040, 1020, and 995(–S–N–); ¹H NMR (CDCl₃) δ=2.35 (3H, s, –C₆H₄CH₃–*p*), 7.22–8.23 (14H, m, aromatic protons); MS (20 eV) *m/z* (rel intensity) 355(M⁺; 9), 264(56), 202([PhSPh]⁺; 100), 186(14), 174(10), 154(36), 138(11), 124(8), and 109(22). Found: C, 64.55; H, 4.76; N, 3.98%. Calcd for C₁₉H₁₇NO₂S₂: C, 64.19; H, 4.82; N, 3.98%.

Preparation of 2d. 2b (600 mg, 1.77 mmol) was dissolved in chloroform. To this solution was added chloramine-*T* (75 mg) in methanol. After stirring the mixture for 30 min at 25 °C, the solvent was removed *in vacuo*, the crude product was separated through column chromatography using chloroform as eluent. The yield was 782 mg, 87% (recrystallized from ethanol). This sulfoximine was also prepared by the reaction of sodium salt of *S,S*-diphenylsulfoximine with *N*-(*p*-tolylsulfonyl)-*p*-toluenesulfinimidoyl chloride in benzene. Yield was 75% (colorless crystals). Mp 118.0–118.5 °C; IR (KBr) 1290(O=S=O), 1280(O=S=O), 1230(O=S–N–), 1140(O=S=O), 1095(O=S–N–), 1085(O=S–N–), 1035 and 955 (S(IV)–N); ¹H NMR (CDCl₃) δ=2.34 (3H, s, –C₆H₄CH₃–*p*), 2.34 (3H, s, –SO₂C₆H₄CH₃–*p*), 7.10–8.12 (18H, m, aromatic protons); MS (20 eV) *m/z* (rel intensity) 508 (M⁺; 2), 369 ([PhS(O) (NS(N)C₆H₄CH₃–*p*)]⁺; 100), 339(8), 202(60), 186(28), 169(12), 155(17), 137(40), 125(39), 124(28), 123(28), 109(18), 91(77), 90(62), and 77(16). Found: C, 61.23; H, 4.66; N, 5.41%. Calcd for C₂₆H₂₄N₂O₃S₃: C, 61.39; H, 4.75; N, 5.50%.

Preparation of 2g. *S,S*-Diphenyl-*N*-chlorosulfoximine which was prepared by the reaction of 2a with sodium hypochlorite in aqueous acetonitrile, was dissolved into chloroform at 25 °C. To this solution was added diphenyl sulfide in chloroform with stirring at 25 °C for 30 min. The mixture was washed with an aqueous solution of sodium perchlorate, with water and dried over magnesium sulfate. Chloroform was removed *in vacuo* and the product was separated by column chromatography using chloroform–methanol (9:1) as an eluent. Recrystallization of this product was performed from ethanol. Yield was 80%; colorless crystals; mp 155.5–156.0 °C. IR (KBr) 1235(O=S–N–), 1100(O=S–N–), 1090(OCIO₃), 1030, and 985(–S–N=); ¹H NMR (CDCl₃) δ=7.23–7.97 (20H, m, aromatic protons). Found: C, 57.49; H, 4.02; N, 2.84%. Calcd for C₂₄H₂₀NO₅S₂Cl: C, 57.42; H, 4.01; N, 2.79%.

Preparation of 2e. The sulfonylation of 2a was

reported earlier.¹⁴ **2c** (300 mg, 0.85 mmol) was dissolved in dichloromethane. To this solution was added a solution of **mCPBA** (220 mg) in dichloromethane. After 2 h of stirring the usual work-up gave the crude product upon column chromatography using chloroform as an eluent. Further purification was carried out by recrystallization from ethanol. Yield was 297 mg, 95%; colorless crystals; mp 137.5 °C.

This sulfoximine was also obtained from the corresponding **2b** by oxidation with 2 equiv of **mCPBA** in dichloromethane. Yield was 99%; IR(KBr) 1295(O=S=O), 1240(O=S=N-), 1150(O=S=O), 1100(O=S=N-), 1065, 1020, and 995(O=S=N-); ¹H NMR (CDCl₃) δ = 2.38 (3H, s, -C₆H₄CH₃-p), 7.13–8.06 (14H, m, aromatic protons); MS (20 eV) *m/z* (rel intensity) 371(M⁺; 12), 294(2), 278(29), 139([PhS(O)N]⁺; 100), and 125(45).

Preparation of 2f. To a dichloromethane solution of **2d** (200 mg, 0.39 mmol) was added a dichloromethane solution of **mCPBA** (9 mg). After 8 h, the reaction mixture was washed with water, aqueous sodium carbonate solution and then washed with water. Dichloromethane solution was dried over magnesium sulfate and the solvent was removed under reduced pressure. The solid obtained was purified through column chromatography using chloroform as an eluent. Further purification was accomplished by recrystallization from ethanol. Yield was 163 mg, 79%; colorless crystals; mp 198.0–198.5 °C; IR(KBr) 1300(O=S=O), 1250(O=S=N-), 1235(O=S=N-), 1140(O=S=N-), 1100(O=S=N-), 1060, 1035, 1005, and 990 (-S=N-); ¹H NMR (CDCl₃) δ = 2.33 (3H, s, -C₆H₄CH₃-p), 2.33 (3H, s, -SO₂C₆H₄CH₃-p), 7.05–7.95 (18H, m, aromatic protons); MS (20 eV) *m/z* (rel intensity) 524(M⁺; 0.9), 447(0.9), 417(1), 385(8), 308(1), 278(11), 264([Ph₂S(O)NSO]⁺; 100), 246(8), 202(6), 200(13), 139(89), 125(27), and 109(2). Found: C, 59.28; H, 4.41; N, 5.20%. Calcd for C₂₆H₂₄N₂O₄S₃: C, 59.52; H, 4.61; N, 5.33(%)

Reaction of 3ae with p-Toluenesulfonyl Chloride. **3ae** (700 mg, 1.9 mmol) and triethylamine (230 mg, 2.3 mmol) were dissolved into dichloromethane (20 mL). To this solution was added dropwise *p*-toluenesulfonyl chloride (300 mg, 1.9 mmol) in dichloromethane (10 mL) at -20 °C under stirring. After the solution was kept for 10 min at -20 °C, the cooling bath was removed and heterogeneous reaction mixture was stirred until the solution was reached at room temperature. After the usual work-up, **1e** (578 mg) was obtained in 86% yield. **3be** was not obtained.

Preparation of 3ce. **3ae** (3.0 g, 8.1 mmol) was dissolved in 30 mL of dichloromethane. To this solution was added dropwise *p*-toluenesulfonyl chloride (1.5 g) and triethylamine (1.1 g) with stirring at -70 °C under cooling with Dry Ice-acetone bath. After stirring for 20 min at 25 °C, the precipitates were filtrated off. The organic solution was washed with water and dried over magnesium sulfate. The crude product thus obtained was recrystallized from dichloromethane-pentane. Yield was 3.5 g (85%); colorless crystals; mp 143.0–144.0 °C; IR(KBr) 1320 (O=SO), 1305(O=S=O), 1185(O=S=O), 1160(-N=S=N-), 1105(-N=S=N-), 1060(-N=S=N-), and 985(-S=N-); ¹H NMR (CDCl₃) δ = 2.34 (3H, s, -S(O)C₆H₄CH₃-p), 2.44 (3H, s, -SO₂C₆H₄C₆H₄CH₃-p), and 7.05–8.27 (18H, m, aromatic protons); MS (20 eV) *m/z* (rel intensity) 354(1), 278(1), 214(1), 200([Ph₂S-N]⁺; 100), 186(10), 139(1), and 123(6). Found: C, 61.56; H, 4.65; N, 5.47%. Calcd for C₂₆H₂₄N₂O₃S₃: C, 61.39; H, 4.75; N, 5.50%.

Preparation of 3ee. Sulfonylation of **3ae** with *p*-toluenesulfonyl chloride in the presence of various bases, such as triethylamine or 2,2,6-trimethylpyridine was not successful, and the original sulfonylimine was recovered nearly quantitatively. However, **3ee** was obtained by another way. To a dichloromethane solution of **3ce** (500 mg, 0.98 mmol) was added a dichloromethane solution of **mCPBA** (2-fold

excess) under cooling at 0 °C with an ice-water bath with stirring. After removing the precipitated *m*-chlorobenzoic acid, the solution was washed with aqueous sodium carbonate, water and dried over magnesium sulfate. The solvent was removed by evaporation, the crude crystals were obtained. Purification was achieved by recrystallization from ethanol. Yield was 485 mg, 94%; colorless crystals, mp 213.5 °C; IR(KBr) 1330(O=S=O), 1165(-N=S=N-), 1080(-N=S=N-), 1050(-N=S=N-), and 995(-S=N-); ¹H NMR (CDCl₃) δ = 2.40 (3H, s, -NSO₂C₆H₄CH₃-p), 2.40 (3H, s, -NSO₂C₆H₄CH₃-p), and 7.11–8.02 (18H, m, aromatic protons). MS (20 eV) *m/z* (rel intensity) 370(5), 306(12), 279(42), 265(47), 215(10), 201(66), 186(78), 171(6), 155(23), 139(15), 119(73), and 91([Tol]⁺; 100). Found: C, 59.97; H, 4.54; N, 5.20%. Calcd for C₂₆H₂₄N₂O₄S₃: C, 59.52; H, 4.61; N, 5.33%.

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