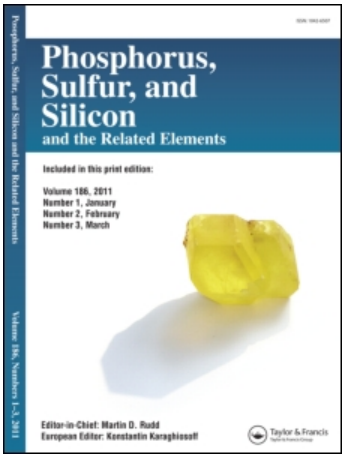

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THERMOLYSES AND REACTIONS WITH NUCLEOPHILES OF *N*-SULFUR-GROUP-SUBSTITUTED SULFOXIMINES

Shigeru Oae[ab]; Kunihiko Akutagawa[a]; Naomichi Furukawa[a]
[a] Department of Chemistry, The University of Tsukuba, Ibaraki, Japan [b] Okayama University of Science, Okayama, Japan

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THERMOLYSES AND REACTIONS WITH NUCLEOPHILES OF *N*-SULFUR-GROUP-SUBSTITUTED SULFOXIMINES

SHIGERU OAE,*[a] KUNIHIKO AKUTAGAWA
and NAOMICHI FURUKAWA*

Department of Chemistry, The University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

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Thermolyses and reactions with nucleophiles of *S,S*-diphenylsulfoximines (**1**) bearing the following *N*-sulfur-substituents, i.e., *N*-*p*-tolylthio-(**b**), *N*-*p*-tolylsulfinyl-(**c**), *N*-(*N'*-*p*-tolylsulfonyl-*p*-toluenesulfinimidoyl)-(**d**), *N*-(*S',S'*-diphenylsulfonio)-(**e**), *N*-*p*-tolylsulfonyl-(**f**), and *N*-(*N'*-*p*-tolylsulfonyl-*p*-toluenesulfonimidoyl)-(**g**), have been examined. The former three sulfoximines (**1b–d**) are thermally unstable and readily decompose to form diphenyl sulfoxide and diphenyl sulfide by the initial cleavage of the *S*—*N* linkage in the original sulfoximines. The latter three sulfoximines (**1e–g**) fairly stable thermally. **1b–d** were found to react with several nucleophiles to afford the corresponding sulfenylated, sulfinylated or sulfinimidoylated products together with *N*-unsubstituted sulfoximine (**1a**). **1e** was found to react with potassium hydroxide/methanol or chloramine-*T*/*N*,*N*-dimethylformamide to afford diphenyl sulfoxide or *S,S*-diphenyl-(*N*-*p*-tolylsulfonyl)sulfilimine along with **1a** in good yields. The latter two sulfoximines (**1f, g**) were found to be inert in the treatment with a few nucleophiles.

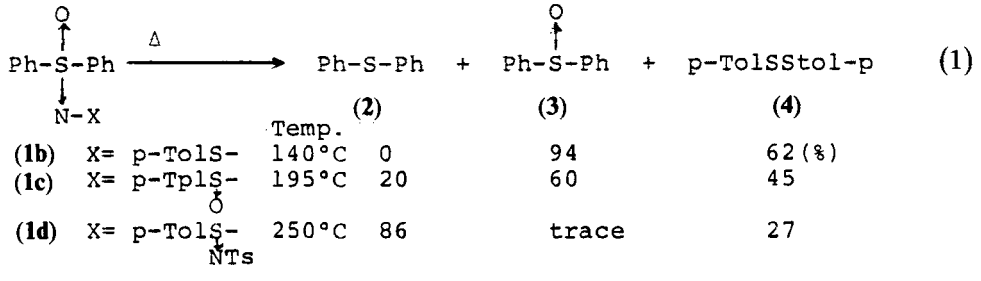
S,S-Diphenyl-(*N*-*p*-tolylthio)-(**1b**), -(*N*-*p*-tolylsulfinyl)-(**1c**), -(*N*-*p*-toluenesulfinimidoyl)-(**1d**), and -*N*-(diphenylsulfonio)-(**1e**) sulfoximines[1] are all new to sulfoximine chemistry[2] and their chemical behavior and reactivity have not been explored. As a preliminary step, thermal decompositions and reactions of these sulfoximines with several nucleophiles have been examined.

RESULTS AND DISCUSSION

Thermal Decomposition of N-Substituted Sulfoximines

Thermal decomposition of these *N*-substituted sulfoximines was carried out under appropriate conditions. The resulting data are listed in Table I.

The sulfoximine, **1b**, **1c**, or **1d** underwent thermal decomposition under relatively mild conditions to give the various reduced products, such as diphenyl sulfide (**2**) or diphenyl sulfoxide (**3**) and di-*p*-tolyl disulfide (**4**), whereas **1e**, **1f**, or **1g** did not decompose at all even upon heating at 250°C or 300°C; the starting materials were recovered (Eqs. (1) and (2))



(1)

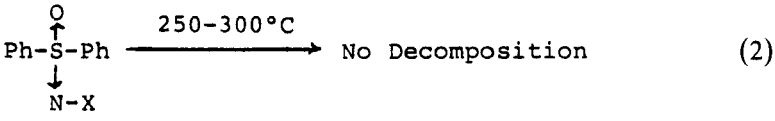
[a]Present address; Okayama University of Science, Ridai-cho, 1-1, Okayama, 700, Japan.

TABLE I

Thermal decompositions of *S,S*-diphenyl-*N*-substituted sulfoximines (**1**)

X	Temp (°C)	Time (min)	Yield (%)[a]				
			Ph-S(O)-Ph (NH)	Ph-S(O)-Ph	Ph-S-Ph	(p-TolS)$_2$	Ph-S(O)-Ph (N-X)
S—Tol-*p* (**1b**)	140	5	0	94	0	62	0
S(O)—Tol-*p* (**1c**)	195	5	0	60	20	45	0
S(O)(NTs)—Tol-*p* (**1d**)	250	2	0	trace	86	27	0
$+OClO_3^-$ S(Ph)—Ph (**1e**)	300	30	0	0	0	0	98
SO_2Tol-*p* (**1f**)	250	60	0	0	0	0	100
S(O)(NTs)—Tol-*p* (**1g**)	250	60	0	0	0	0	100

[a]Isolated yield.
[b]Yields were determined by HPLC.



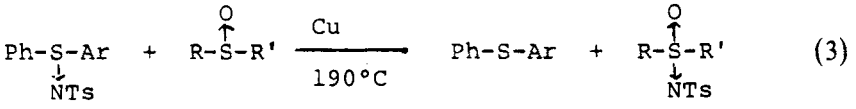
(2)

(**1e**) X=S(Ph)$_2^+$
(**1f**) X=p-TolSO$_2$-
(**1g**) X=p-TolS(O)(NTs)-

Thus, the lower the oxidation state of the sulfur atom in the *N*-substituent of the *N*-substituted sulfoximine, the easier is the thermal decomposition of the sulfoximine. This suggests that the *N*-sulfonyl group in the sulfoximine (**1f**) may strengthen the central sulfinimidoyl *S*(**VI**)—*N* linkage by resonance interaction with the electron-withdrawing sulfonyl group, whereas repulsive interaction between the *N*-*p*-tolylthio sulfur in **1b** with the imino nitrogen would destabilize the *S*(**VI**)—*N* linkage, resulting in the facile thermal decomposition involving *S*—*N* bond cleavage. In the thermal decompositions of these sulfoximines (**1b–d**), the yields of the sulfoxide (**3**) and the disulfide (**4**) increased and those of the sulfide (**2**) decreased, as the oxidation state of the sulfur atom in the *N*-substituent become higher, i.e., in the order of **1b**, **1c**, and **1d**.

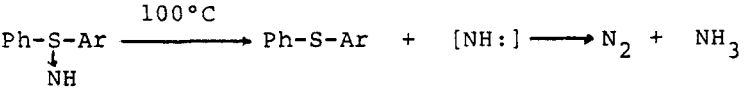
Although sulfilimines have been shown to generate nitrene by *S*(**IV**)—*N* bond fission both thermally[3] and photochemically,[4] diaryl-*N*-sulfonylsulfilimines (**5**) have

been found to react with the sulfoxide (**3**) in the presence of metallic copper upon heating to give the corresponding diaryl sulfides and the sulfoximine (**1f**), *via* formation of an unstable *p*-toluenesulfonylnitrene or a copper–nitrenoid complex[5] (Eq. (3))



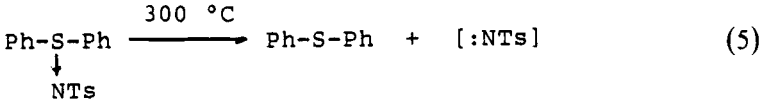
(3)

For example, unsubstituted diphenylsulfilimine decomposes above 100°C to afford the sulfide (**2**) and *N—H* nitrene[6] (Eq. (4))



(4)

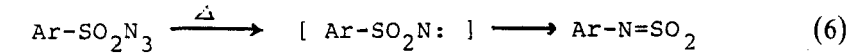
In contrast, diphenyl-(*N*-*p*-tolylsulfonyl)sulfilimine is known to decompose above 300°C to afford the sulfide (**2**) and *p*-toluenesulfonamide and several unidentified products derived from free *p*-toluenesulfonylnitrene[7] (Eq. (5))



(5)

Thus, it is interesting to see whether or not the nitrene is generated in the thermal decomposition of these *N*-substituted sulfoximines.

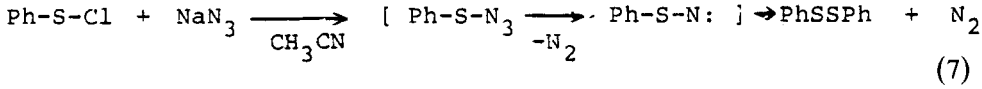
p-Toluenesulfonylnitrene is known to be generated by thermolysis of its azide derivative and to undergo a Curtius-type rearrangement or to insert into C—H bonds similarly to the carbonylnitrene generated from the carbonylazide.[8] However, benzenesulfinylnitrene generated from thermally unstable benzenesulfinylazide has been reported not to undergo the Curtius-type rearrangement nor to insert into C—H bonds, unlike to those generated from the carbonyl- and the sulfonylazide, but instead reacts with dipolar and nucleophilic compounds to give products which are different from those obtained from the carbonyl and the sulfonylazide;[9] (Eq. (6))



(6)

For example, the reaction of benzenesulfinylazide with methyl phenyl sulfoxide yielded *S*-methyl-*S*-phenyl-(*N*-benzenesulfonyl)sulfilimine or *S*,*S*-dimethyl-(*N*-benzenesulfonyl)sulfilimine rather than *S*-methyl-*S*-phenyl-(*N*-benzenesulfinyl) sulfoximine or dimethyl-(*N*-benzenesulfinyl)sulfoximine.

On the other hand, *p*-toluenesulfenylnitrene is not yet known since *p*-toluenesulfenylazide, the source of the nitrene, is so unstable that it cannot be isolated, nor can exist even in solution; the sulfenyl azide once formed would undergo self decomposition to afford the corresponding disulfide and nitrogen[12] (Eq. (7))



(7)

(1b) (1c)

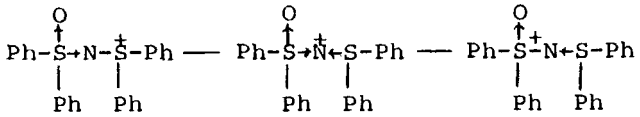
FIGURE 1 The repulsive "rabbit ears effect" of *S,S*-diphenyl-(*N*-*p*-tolylthio)sulfoximine (**1b**) and -(*N*-*p*-tolylsulfinyl)sulfoximine (**1c**).

Therefore, **1b** which was isolated as relatively stable pale yellow crystals, is considered to be a good source for generating *p*-toluenesulfenylnitrene. However, when **1b** was treated with cyclohexene at 140°C for 30 min in a sealed tube, no adduct derived from the *p*-toluenesulfenylnitrene was obtained but the sulfoxide (**3**) and the disulfide (**4**) were obtained in 90 and 55% yields respectively. The sulfoximine (**1c**) is quite stable and did not decompose below 195°C. However, when thermal decomposition of **1c** which is presumed to be a good source of the sulfinylnitrene, was carried out in dimethyl or methyl phenyl sulfoxide, at 200°C for 30 min, no *N*-*p*-tolylsulfonylsulfilimine, the possible *p*-toluenesulfinylnitrene trapped product, was obtained. Since *S,S*-dialkyl- or *S*-alkyl-*S*-aryl-*N*-(*p*-tolylsulfonyl)-sulfilimines have been shown to react with such sulfoxides as dimethyl and methyl phenyl sulfoxides at around 200°C to afford the disulfides formed by *C*—*S*(**IV**) bond fission of the starting sulfilimines,[10] *N*-*p*-tolylsulfonylsulfilimine once formed in the present reaction would have reacted further with dimethyl or methyl phenyl sulfoxide and therefore could not be identified at relatively high reaction temperature as in the similar thermolysis of other sulfilimines with dimethyl sulfoxide.[10]

The Curtius-type rearrangement product such as toluidine was not obtained. The facile cleavage of the *S*—*N* linkage in **1b** is undoubtedly due to the repulsive "rabbit ears effect" between the imino nitrogen and the sulfenyl sulfur atoms as illustrated in Figure 1.

Even in **1c**, the similar repulsive interaction, though small, between the imino nitrogen and the sulfinyl sulfur atoms would be in operation to assist the cleavage of the *S*—*N* linkage. In the case of **1e**, there is little repulsive interaction but a sufficient delocalization of the lone-pair electrons into the positively charged sulfonio sulfur atom to strengthen the *S*—*N* linkage, as shown below (Figure 2).

Decomposition did not proceed even with heating at 300°C for 30 min. Such a thermally stable azasulfonium salt has not been previously described.[11] **1f** also did not decompose by heating at 250°C for 60 min. In the mass spectrum of **1f** there is a base peak generated by the *C*—*S* bond cleavage similar to that of the sulfone,



(1e)

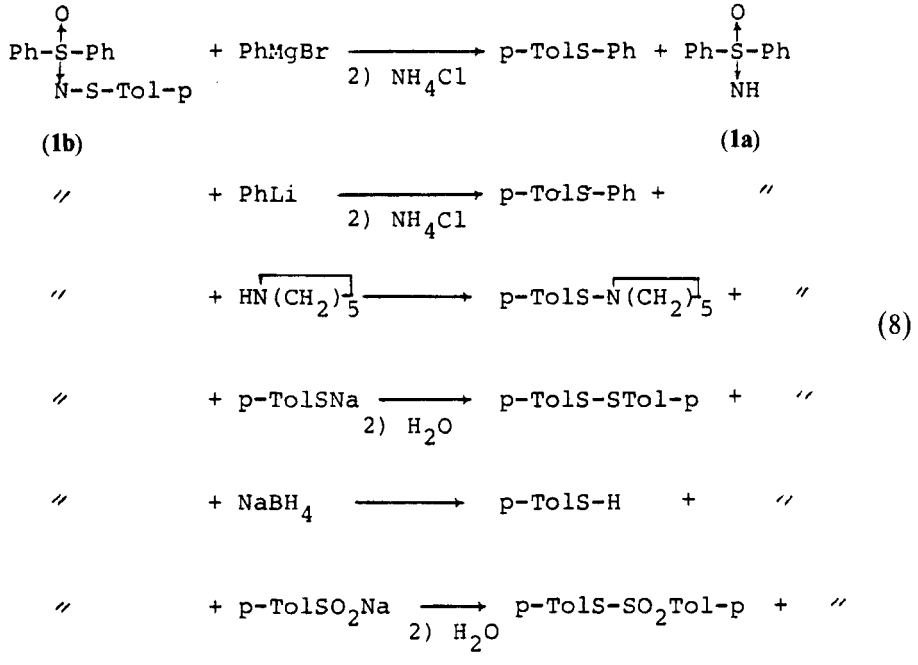
FIGURE 2 Delocalization of *S,S*-diphenyl-(*S'S'*-diphenylsulfonio)sulfoximine (**1e**).

however, no peak of $[Ph—S(O)—Ph]^+$; derived by the *S*(Sulfoximine)-*N* bond fission, was observed.

Reaction of N-Substituted Sulfoximines (**1**) *with Several Nucleophiles*

S,S-Diphenyl-(N-p-tolylthio)sulfoximine (**1b**)

1b has been treated with several nucleophiles under appropriate conditions. This reactive sulfoximine has been found to react with various nucleophiles such as phenylmagnesium bromide, phenyllithium, piperidine, sodium *p*-toluenethiolate, sodium borohydride and sodium *p*-toluenesulfinate, to give the corresponding sulfenylated compounds, i.e., the sulfides, the sulfenamide, the disulfide, the thiol and the thiolsulfonate in good yields together with the desulfenylated **1a** after the usual work-up process (Eq (8))



(8)

TABLE II

Products formed in the reaction of *S,S*-diphenyl-(*N*-*p*-tolythio)sulfoximine (**1b**) with various nucleophiles

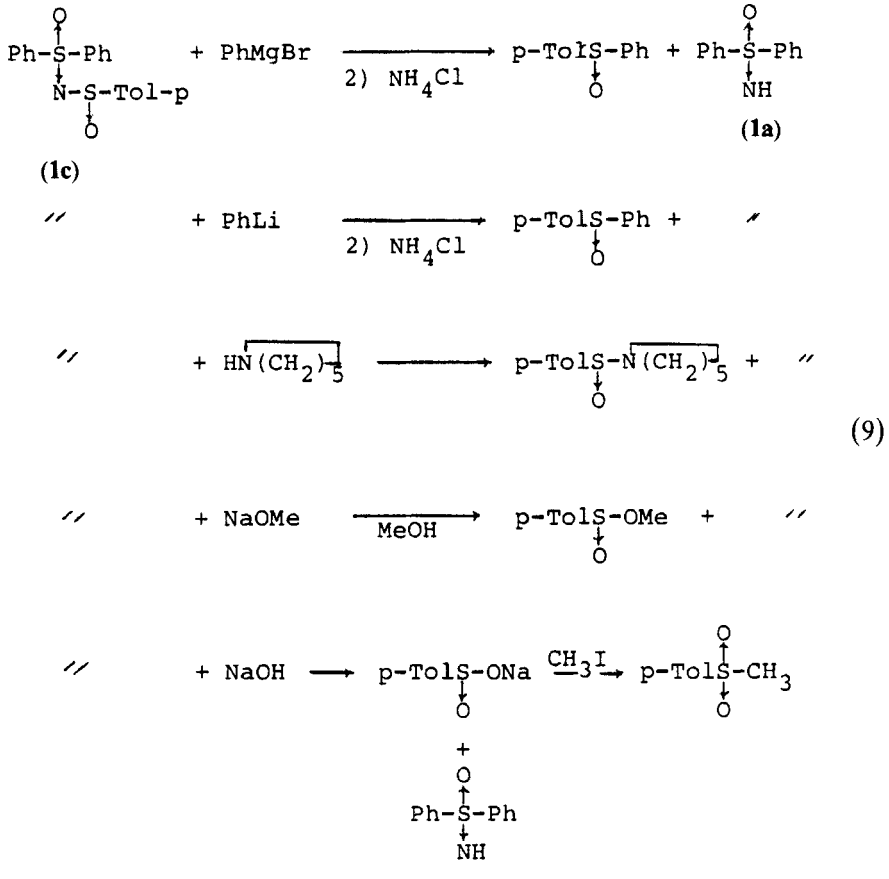
Nucleophile	Solvent	Temp (°C)	Time (min)	Product	Yield (%)[a]
PhMgBr (1.2 eq)	THF	−50 → 25	20	*p*-TolS—Ph	97
p-TolMgBr (1.2 eq)	THF	−50 → 25	20	*p*-TolS—Tol-*p*	98
PhLi (1.2 eq)	THF	−70 → 25	30	*p*-TolS—Ph	83
$HN(CH_2)_5$ (2.5 eq)	CH_2Cl_2	25	60	*p*-TolS—$N(CH_2)_5$	75
p-TolSNa (1.0 eq)	MeOH	25	10	*p*-TolS—STol-*p*[b]	96
p-$TolSO_2Na$ (3.0 eq)	DMF	25	180	*p*-TolS—SO_2Tol-*p*	80

[a] Isolated yield.
[b] Yield was determined by HPLC.

The results thus obtained are summarized in Table II. Thus, **1b** was found to be a good sulfenylating reagent.

S,S-Diphenyl-(N-p-tolylsulfinyl)sulfoximine (**1c**)

1c has also been found to react with various nucleophiles, e.g., phenylmagnesium bromide, phenyllithium, piperidine, sodium methoxide, sodium hydroxide, to give the corresponding sulfinylated products such as the sulfoxide, the sulfinamide, the sulfinic ester, and the sulfinic acid (as methyl *p*-tolyl sulfone), together with the desulfinylated **1a** after the usual work-up process (Eq. (9))



(9)

The results thus obtained are listed in Table III. Thus, **1c** was also found to be a good sulfinylating reagent.

N-(N'-p-tolylsulfonyl)-p-toluenesulfinimidoylsulfoximine (**1d**)

1d was found to react with a few nucleophiles to give the corresponding sulfonimidoylated products in good yields along with the desulfonimidoylated **1a** after the

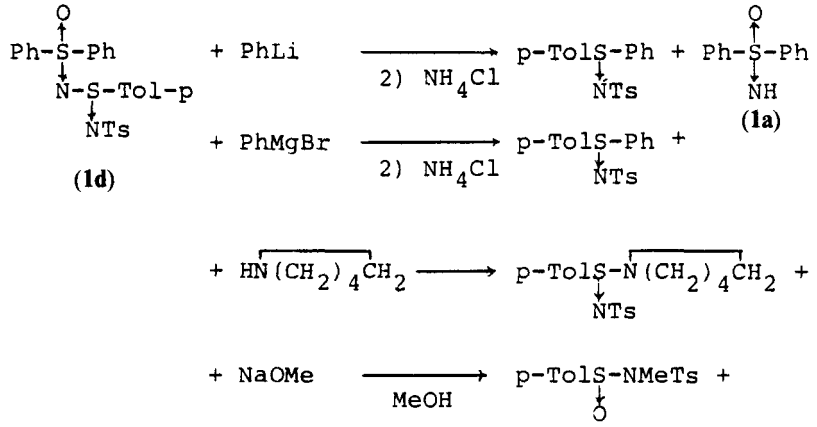
TABLE III

Products formed in the reaction of *S,S*-diphenyl-(*N*-*p*-tolylsulfinyl)sulfoximine (**1c**) with various nucleophiles

Nucleophile	Solvent	Temp (°C)	Time (min)	Product	Yield (%)[a]
PhMgBr (1.2 eq)	THF	−50 → 25	30	*p*-TolS(O)—Ph	67
p-TolMgBr (1.2 eq)	THF	−50 → 25	30	*p*-TolS(O)—Tol-*p*	72
PhLi (1.2 eq)	THF	−70 → 25	30	*p*-TolS(O)—Ph	75
MeMgBr (1.2 eq)	THF	−50 → 25	30	*p*-TolS(O)—Me	60
HNMePh (3.0 eq)	CH_2Cl_2	25	60	*p*-TolS(O)—NMePh	75
$HN(CH_2)_4CH_2$ (2.5 eq)	CH_2Cl_2	25	60	*p*-TolS(O)—$N(CH_2)_4CH_2$	77
$HNEt_2$ (2.0 eq)	CH_2Cl_2	25	60	*p*-TolS(O)—NEt_2	81
NaOMe (1.5 eq)	MeOH	25	60	*p*-TolS(O)—OMe	85
NaOH (3.0 eq)	$MeOH/H_2O$	25	30	[*p*-TolS(O)—ONa]	—
	(2) MeI	25	30	*p*-$TolSO_2$—Me	78

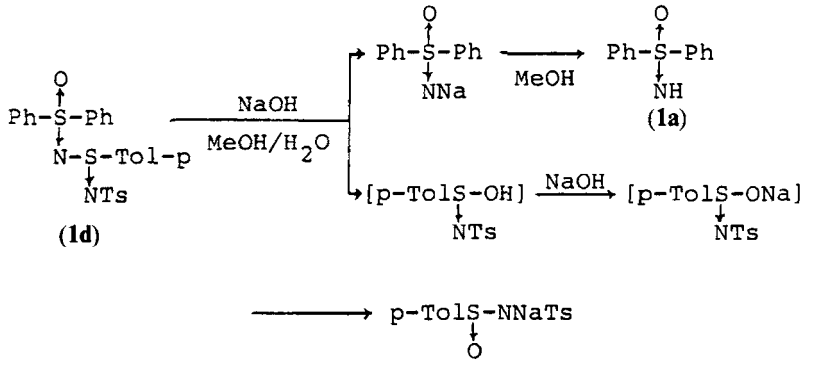
[a]Isolated yield.

usual work-up process (Eq. (10))



(10)

Alkaline hydrolysis of **1d** gave the sodium salt of *N*-*p*-toluenesulfonyl *p*-toluenesulfinimide, apparently through the attack of hydroxide ion on the sulfinimidoyl sulfur atom. The results thus obtained are listed in Table IV (Eq. (11))



(11)

TABLE IV

Products formed in the reaction of *S,S*-diphenyl *N*-(*N'*-*p*-tolysulfonyl)-*p*-toluenesulfinimidoylsulfoximine (**1d**) with a few nucleophiles

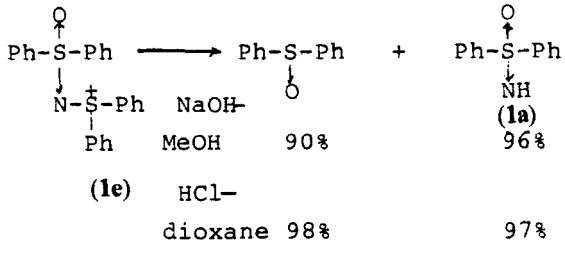
Nucleophile	Solvent	Temp (°C)	Time (min)	Product	Yield (%)[a]
PhMgBr (1.2 eq)	THF	−50 → 25	40	*p*-TolS(NTs)—Ph	70
PhLi (1.2 eq)	THF	−70 → 25	30	*p*-TolS(NTs)—Ph	60
$HN(CH_2)_4CH_2$ (2.5 eq)	CH_2Cl_2	25	80	*p*-TolS(NTs)—$N(CH_2)_4CH_2$	54
NaOMe (1.5 eq)	MeOH	25	60	*p*-TolS(O)NMeTs	76
NaOH (3.0 eq)	MeOH/H_2O	25	60	*p*-TolS(O)NNaTs	86

[a] Isolated yield.

1d was also found to be a good sulfinimidoyl-group transfer reagent. However, **1f** and **1g** are quite inert to these nucleophiles even under much harder conditions and the starting sulfoximine was recovered.

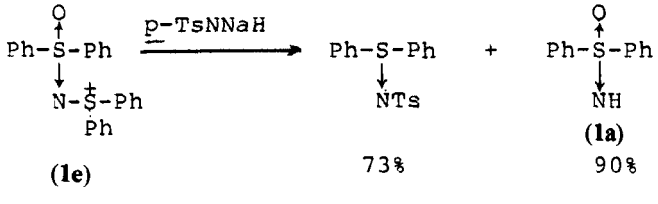
S,S-Diphenyl-N-(diphenylsulfonio)sulfoximine Perchlorate (**1e**)

Both alkaline and acid hydrolysis of the title sulfoximine (**1e**) was carried out under appropriate conditions, and gave the sulfoxide (**3**) derived from the sulfonio moiety and **1a** derived from the sulfoximino part in good yields (Eq. (12))



(12)

The *N*-sulfoniosulfoximines were found to react with sodium methoxide/methanol, or sodium salt of *p*-toluenesulfonamide/*N,N*-dimethylformamide to afford the corresponding sulfoxide or the *N*-*p*-tolylsulfonylsulfilimine along with the desulfonioated sulfoximine after the usual work-up process (Eq. (13))



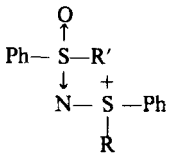
(13)

The results are summarized in Table V.

Treatment of **1e** with a few other nucleophiles such as sodium borohydride, tetra-*n*-butylammonium iodide, sodium benzenethiolate, sodium cyanide, triphenylphosphine, sodium azide afforded the sulfide (**2**) derived from the sulfonio part and

TABLE V

Products formed in the acid and base-catalyzed hydrolysis of *S,S*-diphenyl-*N*-(*S'*,*S'*-sulfonio)sulfoximine

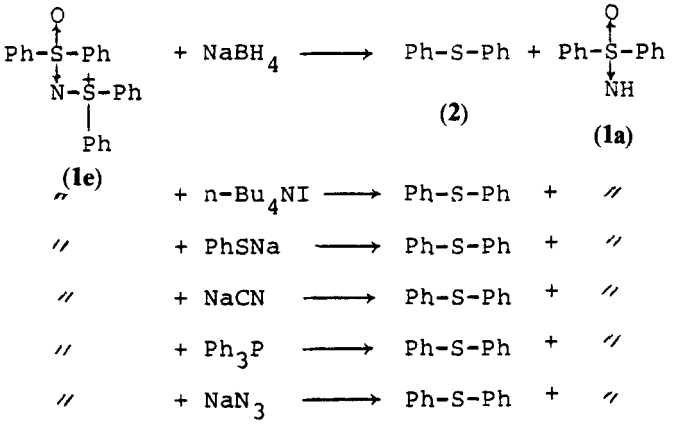


→ Products

R	R'	Nucleophile/Solvent	Temp (°C)	Time (hr)	Yield (%)[a] PhSR (O)	Yield (%)[a] PhSR' (NH)
Ph	Ph	KOH/80% MeOH	20	1	90	96
Me	Ph	KOH/80% MeOH	20	1	92	95
Ph	Me	KOH/80% MeOH	20	1	90	97
Me	Me	KOH/80% MeOH	20	1	95	99
Ph	C_6H_4OMe-*o*	KOH/80% MeOH	20	1	91	95
Ph	C_6H_4OMe-*o*	KOH/80% MeOH	20	1	93	94
Ph	Ph	10% HCl aq/dioxane	25	2	98	97
Ph	Ph	10% $HClO_4$ aq/dioxane	25	2	92	95
Ph	Ph	10% H_2SO_4 aq/dioxane	25	2	94	93
Me	Ph	10% HCl aq/dioxane	25	2	90	98
Ph	Ph	(1) conc. H_2SO_4/(2) NaOH aq.	25	24	97	98
Ph	Ph	NaOMe/MeOH	25	4	87	94
Me	Ph	NaOMe/MeOH	25	3	91	93
Ph	Ph	NaNHTs/DMF	80	4	73 (PhS(NTs)Ph)	90
Me	Ph	NaNHTs/DMF	80	4	65 (PhS(NTs)Me)	93

[a]Isolated yield.

1a derived from the sulfoximino part in good yields (Eq. (14))

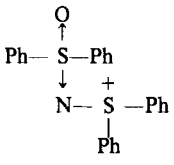


(14)

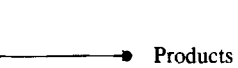
The results are listed in Table VI.

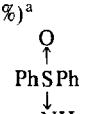
TABLE VI

Products formed in the reaction of *S,S*-diphenyl-*N*-(*S',S'*-diphenylsulfonio)-sulfoximine (**1e**) with several nucleophiles



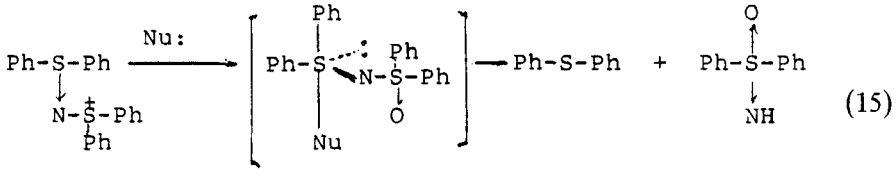
(**1e**)



Nucleophile	Solvent	Temp (°C)	Time (hr)	Yield (%)[a] PhSPh	Yield (%)[a] 
$NaBH_4$ (2.5 eq)	EtOH	20	5 min	99	96
n-Bu_4NI (3.0 eq)	$CHCl_3$	50	1	65	58
PhSNa (2.0 eq)	$CHCl_3$	20	5 min	78	80
NaCN (2.0 eq)	DMF	200	5	90	—
Ph_3P (2.0 eq)	DMF	200	5	85	—
NaN_3 (3.0 eq)	DMF	200	5	83	—

[a]Isolated yield.

Apparently the nucleophiles attack the sulfonio sulfur atom to form an incipient sulfurane which eventually collapses to give the product, as shown below (Eq. (15))



(**1e**) (**1a**) (15)

Further study is necessary to understand the detailed mechanisms.

EXPERIMENTAL

General. Melting points of the products were measured in a Yanaco instrument and were uncorrected. IR spectra were taken with a Hitachi 215 spectrophotometer. ^1H NMR spectra of all the compounds were obtained with a Hitachi Perkin-Elmer R-20 spectrometer in 20% solutions of $CDCl_3$ using tetramethylsilane as the internal standard. Liquid chromatographs were obtained with a Yanaco-L-1030 instrument using methanol as the eluent. Thin-layer chromatography was carried out with Merck DC-Plastikofolien Kieselgel 60 F 254 Art. 5735 with fluorescent indicator using various solvents and mixed solvents as eluents. Development was followed with UV light or by coloring with iodine. Silica gel used for column chromatography was either Wako or Merck chromatographic grade. Anhydrous acetonitrile, tetrahydrofuran, and benzene were obtained by the usual procedures. Other chemicals were of reagent grade.

Materials. *S,S*-Diphenyl-(*N*-substituted)sulfoximines (**1b–g**) were prepared by the method reported earlier.[1]

Thermal decomposition of **1b**. In a typical run, **1b** (300 mg) was placed into a 30 ml round bottomed flask and was heated at 140°C for 5 min under N_2 atmosphere. After the reaction was finished, the reactor was cooled with water, and the pale yellowish oily product was obtained. This oily product mixture was separated by column chromatography using mixed solvent, benzene/hexane = 2/1, as the eluent. The products thus obtained and identified by comparing their GLC, HPLC behavior and IR spectra with those of authentic samples, were di-*p*-tolyl disulfide (62%) and diphenyl sulfoxide (94%) along with several unidentified materials.

Thermal decomposition of **1c**. In a typical run, **1c** (350 mg) was placed into a 30 ml round bottomed flask and was heated at 195°C for 5 min. After the reaction, the reactor was cooled to 25°C by an ice-water bath and a dark brown oily product was obtained. This oily product was separated by column chromatography using mixed solvent, benzene/hexane = 2/1 as an eluent. The products thus obtained identified by comparing their GLC, HPLC behavior and IR spectra with those of the authentic samples were a mixture of di-*p*-tolyl disulfide (**4**), diphenyl sulfide (**2**), and diphenyl sulfoxide (**3**) (60%) and several basic unidentified products. The yields of **2** (20%) and **4** (45%) were determined by HPLC.

Reaction of **1b** *with phenylmagnesium bromide*. To a solution of phenylmagnesium bromide (1.8 mmol) in tetrahydrofuran was added a tretahydrofuran solution of **1b** (1.5 mmol) under cooling at −50°C. After the addition of the sulfoximine, the cooling bath was removed and the reaction mixture was stirred for 20 min. To this solution was added water and then saturated ammonium sulfate. The reaction mixture was transferred into a separatory funnel and the organic layer was washed with 6N HCl aqueous solution three times, and dried over anhydrous magnesium sulfate. The solution was filtered through silica gel using a mixed solvent, benzene/hexane = 1 : 1. The solvent was removed under reduced pressure, and phenyl *p*-tolyl sulfide was obtained as a colorless oil in 97% yield. The water layer was made alkaline with aqueous sodium hydroxide solution, again extracted with chloroform three times, and then the chloroform extract was dried over anhydrous magnesium sulfate. After the solvent was removed *in vacuo*, **1a** was obtained (92%) as a white precipitate which was then recrystallized from benzene for recycled use.

The reactions with *p*-tolylmagnesium bromide, phenyllithium, piperidine, sodium *p*-toluenethiolate, and sodium *p*-toluenesulfinate were performed similarly.

Reaction of **1c** *with phenylmagnesium bromide*. To a solution of **1c** (1.3 mmol) in tetrahydrofuran was added the solution of phenylmagnesium bromide (1.7 mmol) in tetrahydrofuran under cooling at −50°C. After the addition of the Grignard reagent was complete, the reaction mixture was kept stirring for 30 min under cooling at the same reaction condition. The cooling bath was removed and the reaction mixture was allowed to reach at room temperature and then was stirred for 10 min. To this solution was added water and then aqueous saturated ammonium sulfate solution. The reaction mixture was transferred into a separatory funnel and was extracted with chloroform. The organic layer was washed with 6N HCl aqueous solution three times, and was washed with water twice and then dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo*. Purification was accomplished by column chromatography using chloroform as an eluent. Phenyl *p*-tolyl sulfoxide was obtained as colorless crystals in 67% yield. **1a** was also recovered after the usual work-up.

The reactions with *p*-tolylmagnesium bromide, methylmagnesium bromide, phenyllithium, methylaniline, piperidine, diethylamine, sodium methoxide, and sodium hydroxide were performed similarly.

Reaction of **1d** *with phenylmagnesium bromide*. To a solution of **1d** (1.0 mmol) in tetrahydrofuran was added the tetrahydrofuran solution of phenylmagnesium bromide (1.3 mmol) under cooling at −50°C. After the addition of the Grignard reagent, the reaction mixture was kept for 30 min under the same reaction condition and the solution was allowed to reach at room temperature and was stirred for 10 min. To this solution was added water and then aqueous saturated ammonium sulfate. The mixture was transferred into a separatory funnel and was extraced with chloroform. The organic layer was washed with 6N HCl aqueous solution three times, and washed with water and then dried over anhydrous magnesium sulfate. Purification was accomplished by column chromatography using chloroform as an eluent. *S*-Phenyl-*S*-*p*-tolyl-(*N*-*p*-tolylsulfonyl)sulfilimine was obtained as colorless crystals in 60% yield. **1a** was also recovered after the usual work-up.

The reactions with phenyllithium, piperidine, sodium methoxide and sodium hydroxide were performed similarly.

Alkaline hydrolysis of **1e**. To a solution of **1e** (1.5 mmol) in methanol (5 ml) at room temperature a solution of sodium hydroxide (6.0 mmol) in methanol (5 ml) was added. The mixture was stirred at this temperature for 1 h. TLC (silica-gel, chloroform or chloroform/methanol = 4/1), and HPLC of the reaction mixture showed the presence of diphenyl sulfoxide (**3**) and **1a** after disappearance of the starting sulfoximine (**1e**). The reaction mixture was poured into water (20 ml) and then the aqueous solution was

extracted with chloroform (3 × 10 ml) and then was washed with water. The extract was washed with aqueous 6N HCl solution, and was washed with water and then dried over anhydrous magnesium sulfate. After the solvent was removed *in vacuo*, diphenyl sulfoxide (**3**) was obtained in 90% yield as a white precipitate which was then recrystallized from benzene-hexane. The aqueous layer was made alkaline with sodium hydroxide, and was extracted with chloroform and then dried over anhydrous magnesium sulfate. After the solvent was removed *in vacuo*, **1a** was obtained in 96% as white precipitates which were then recrystallized from benzene for recycled use.

Other alkaline hydrolyses of the title sulfoximine were performed similarly.

Acid hydrolysis of **1e**. To a solution of **1e** (1.0 mmol) in dioxane (5 ml) at room temperature, a 10% aqueous solution of HCl (5 ml) was added. The mixture was stirred at room temperature for 3 h. TLC (silica-gel, chloroform or chloroform/methanol = 4/1), and HPLC of the reaction mixture showed the presence of diphenyl sulfoxide (**3**) and **1a** after disappearance of the starting sulfoximine (**1e**). A 6N aqueous HCl solution (10 ml) was added into the reaction mixture and the mixture was extracted with chloroform twice. The organic layer thus obtained was washed with water twice and then dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo*. Diphenyl sulfoxide (**3**) was obtained in 98% yield as a white precipitate which was then recrystallized from benzene-hexane. The aqueous layer was made alkaline with sodium hydroxide, and then was extracted with chloroform. The chloroform solution was washed with water twice and then dried over anhydrous magnesium sulfate. After the solvent was removed *in vacuo*, **1a** was obtained in 97% yield as a white precipitate which was then recrystallized from benzene for recycled use.

Other acid hydrolyses of the title sulfoximine were performed similarly.

Reaction of **1e** *with sodium borohydride*. To a solution of **1e** (1.1 mmol) in ethanol (10 ml) was slowly added a sodium borohydride (2.5 mmol) at 0°C by ice-water bath. After the addition of the sodium borohydride was completed, the reaction mixture was allowed to reach at room temperature, and then was kept stirring for 5 min. After the reaction was finished, the usual work-up was carried out. Diphenyl sulfide (**2**) and **1a** were obtained in 99 and 96% yields respectively.

Reactions with tetra-*n*-butylammonium iodide, sodium benzenethiolate, sodium cyanide, triphenylphosphine, and sodium azide were performed similarly.

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