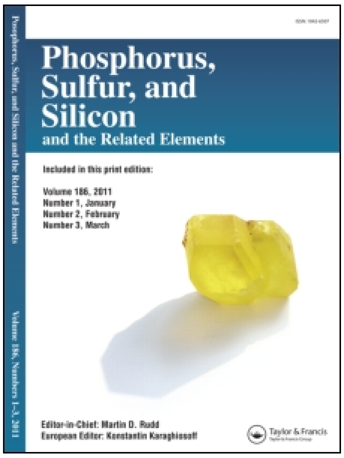

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

COPPER CATALYZED REACTIONS OF *S,S*-DIARYL-*N*-TOSYLSULFILIMINES WITH SULFOXIDES: NEW SYNTHESIS OF *N*-TOSYLSULFOXIMINES

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To cite this Article Akutagawa, Kunihiko , Furukawa, Naomichi and Oae, Shigeru(1984) 'COPPER CATALYZED REACTIONS OF *S,S*-DIARYL-*N*-TOSYLSULFILIMINES WITH SULFOXIDES: NEW SYNTHESIS OF *N*-TOSYLSULFOXIMINES', Phosphorus, Sulfur, and Silicon and the Related Elements, 19: 2, 213 — 221

To link to this Article: DOI: 10.1080/03086648408077582

URL: http://dx.doi.org/10.1080/03086648408077582

Phosphorus and Sulfur, 1984, Vol. 19, pp. 213–221
0308-664X/84/1902-0213/$18.50/0

COPPER CATALYZED REACTIONS OF *S*,*S*-DIARYL-*N*-TOSYLSULFILIMINES WITH SULFOXIDES: NEW SYNTHESIS OF *N*-TOSYLSULFOXIMINES

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(*Received September 23, 1983; in final form November 14, 1983*)

S,*S*-Diaryl-*N*-tosylsulfilimines were readily reduced by treatment with copper to give the corresponding sulfides and a copper–tosylnitrenoid–complex which upon reacting with sulfoxides afforded the corresponding *N*-tosylsulfoximines, derived from sulfoxides in fair yields. When optically active (−)-(*S*)-methyl phenyl sulfoxide was used, the corresponding (+)-*N*-tosylsulfoximine was obtained together with the sulfide derived from the *N*-tosylsulfilimine. The stereochemical course of the conversion of (−)-(*S*)-sulfoxide to (+)-*N*-tosylsulfoximine was found to be mainly retention (76%) with partial racemization due to thermal pyramidal inversion of the starting sulfoxide.

S-Alkyk-*S*-aryl- (**1**) or *S*,*S*-dialkyl-*N*-tosylsulfilimines (**2**) have been shown to react with various nucleophiles.[1-4] However, *S*,*S*-diaryl-*N*-tosylsulfilimines (**3**) did not react with these nucleophiles under the same conditions except in the reaction of **3** with Grignard reagent such as phenylmagnesium bromide[5] which affords the coupling product through a σ-sulfurane. *S*,*S*-Diphenyl-*N*-tosylsulfilimine (**3a**) was shown not to undergo hydrolysis upon treatment with potassium hydroxide in aqueous methanol. However, it reacted with potassium hydroxide in refluxing toluene in the presence of 18-crown-6 as a catalyst, affording both the reduced diphenyl sulfide and the sulfoxide.[6] Recently, "Nucleophilic Oxidation"[7] of several *N*-arenesulfonylsulfilimines with sodium hypochlorite in ethyl acetate–water two phase system in the presence of a quaternary ammonium salt, e.g., tetra-*n*-butylammonium chloride, as a catalyst, was shown to afford the corresponding sulfoximines in excellent yields.[8] Meanwhile, sulfilimines (**1**) has been shown to react with dimethyl sulfoxide (DMSO), to afford methyl phenyl disulfide as the main product, which is considered to be formed by the nucleophilic attack of the oxygen atom of DMSO on the α-carbon atom attached to the sulfinimidoyl sulfur atom of the sulfilimine. When alkyl aryl or diaryl sulfoxides were treated with *N*-tosylsulfilimines, both sulfoxides and sulfilimines were reduced to the corresponding sulfides along with the formation of ammonium *p*-toluenesulfonate, both in substantial yields.[9]

In the course of the studies on the chemistry of sulfilimines, we found that *N*-tosylsulfilimines were reduced quite readily by treatment with metallic copper to afford the corresponding sulfides. When the reduction was carried out in the

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presence of sulfoxides, *N*-tosylsulfoximines derived from sulfoxides were obtained in moderate yields, together with quantitative formation of reduced sulfides. This process seems to involve the initial formation of a complex between copper and the sulfilimine to give incipiently the nitrenoid-copper-complex, which can be trapped with sulfoxides. A few trapping experiments of nitrenes photochemically generated from sulfilimines have been known,[10] whereas those of nitrenes from thermal reactions have not been reported.

This paper describes the reduction of *N*-tosylsulfilimines with copper metal and the reactions of *N*-tosylsulfilimines with sulfoxides in the presence of metallic copper to afford the *N*-tosylsulfoximines from sulfoxides.

RESULTS AND DISCUSSION

Reduction of S,S-Diaryl-N-tosylsulfilimines (3) with Metallic Copper

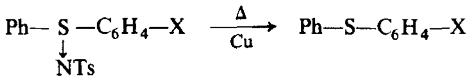
Although sulfilimines (**3**) have been known to be reduced with several reducing agents,[11] reduction using metal has not been carried out. One example of the deoxygenation of such tricoordinate sulfur compounds as thiolsulfonate and sulfoxide with metallic iron was reported earlier by Fujisawa, *et al.*,[12] who also reported that a metal such as copper did not reduce the thiolsulfonate, which however, underwent desulfonylation to afford the corresponding sulfide.[13]

The reagent that was successfully employed in this reduction is readily available powdered copper. Sulfilimines (**3**) were treated with powdered copper at 190°C for 1 h under N_2 atmosphere. The products obtained were found to be the corresponding diaryl sulfides and tosylamide as major products, at 100% conversion of the starting **3**. The results obtained are listed in Table I.

The data indicate that only the cleavage of the *S*(**IV**)—*N* linkage of the sulfilimine was observed in this reaction and no fission of the *C*—*S*(**IV**) linkage took place, unlike the reaction of sulfilimines (**1, 2**) having a *S*(**IV**)—*C*(alkyl) linkage. In the absence of copper, **3** did not decompose even upon heating at 200°C for 24 h.

TABLE I

Reduction of *N*-tosylsulfilimines with metallic copper



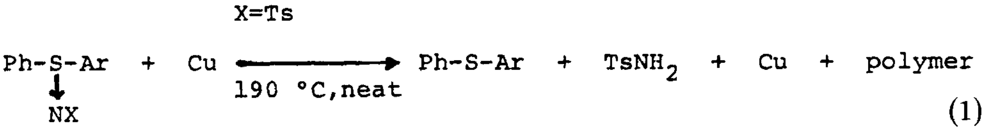
$$\underset{\substack{\downarrow \\ \mathrm{NTs}}}{\mathrm{Ph{-}S}}{-}C_6H_4{-}X \xrightarrow[\mathrm{Cu}]{\Delta} \mathrm{Ph{-}S{-}}C_6H_4{-}X$$

Sulfilimine X	Temp (°C)	Time (min)	Sulfide yield (%)[a]
—H-*p*	190	30	93
—Cl-*p*	190	20	89
—NO_2-*p*	190	10	90
—Me-*p*	200	60	85
—OMe-*p*	200	60	80
—Br-*p*	190	15	94
—OMe-*o*	200	60	85

[a] Isolated yield.

However, it decomposed upon heating at 300°C.[14] Even in the presence of copper the reaction hardly occurred when the reaction temperature was lower than 180°C. The use of solvent also retarded the reaction. Electron-withdrawing substituents such as the nitro group accelerated the reaction. *S*-*o*-Methoxyphenyl-*S*-phenyl-*N*-tosylsulfilimine was also reduced readily to the corresponding sulfide. On the other hand, the reaction of **1** or **2** with copper proceeded less readily than the diaryl derivatives (**3**) and resulted in partial *C*—*S* bond fission along with the concomitant reduction. The isoelectronic sulfoxide, e.g. diphenyl sulfoxide, did not react with copper even heating at 200°C for 12 h.

Generally, *N*-unsubstituted dialkylsulfilimines (**4**) are known to be rather unstable, and decompose even at room temperature,[15] whereas, *N*-unsubstituted diarylsulfilimines (**5**) are thermally stable and do not decompose even upon heating in refluxing benzene for 24 h. *N*-Unsubstituted diphenylsulfilimine (**5a**) decomposes only on heating neat above 100°C to afford the corresponding diphenyl sulfide, N_2 and NH_3, which are assumed to arise by disproportionation of unstable free nitrene formed as an intermediate.[16] However, sulfilimine **5a** has been found to react with copper below 100°C, affording diphenyl sulfide in a quantitative yield. Thus, metallic copper appears to be a useful reducing reagent for reduction of both *N*-unsubstituted and *N*-tosyl-diarylsulfilimines (**5** and **3**) because of the easy work-up (Eq. (1))



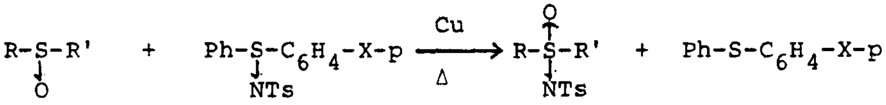
$$\underset{\substack{\downarrow\\ \text{NX}}}{\text{Ph-S-Ar}} + \text{Cu} \xrightarrow[\text{190 °C,neat}]{\text{X=Ts}} \text{Ph-S-Ar} + \text{TsNH}_2 + \text{Cu} + \text{polymer} \qquad (1)$$

X; $p\text{-}CH_3C_6H_4SO_2$(Ts) (**3**)

X; H (**5**)

Reaction of N-Tosylsulfilimines with Sulfoxides in the Presence of Metallic Copper

The reaction of sulfilimines (**3**) with various kinds of sulfoxides in the presence of copper gave the corresponding *N*-tosylsulfoximines which are derived from the sulfoxides, together with diaryl sulfides in moderate yields. During the reaction, the color of the solution changed to deep green initially. The products thus formed were isolated and their structures were established by comparing the spectral data with those of authentic samples. The results are summarized in Table II (Eq. (2))



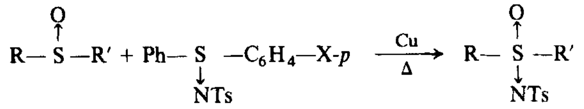
$$\underset{\substack{\downarrow\\ \text{O}}}{\text{R-S-R}'} + \underset{\substack{\downarrow\\ \text{NTs}}}{\text{Ph-S-C}_6\text{H}_4\text{-X-p}} \xrightarrow[\Delta]{\text{Cu}} \underset{\substack{\downarrow\\ \text{NTs}}}{\overset{\substack{\text{O}\\ \uparrow}}{\text{R-S-R}'}} + \text{Ph-S-C}_6\text{H}_4\text{-X-p} \qquad (2)$$

X: H, Cl, CH_3, NO_2

In the absence of copper, however, the reaction of *N*-tosylsulfilimines with sulfoxides was not observed at all under the reaction condition. Although the sulfoxide was

TABLE II

Preparation of *N*-tosylsulfoximines



$$R-\overset{O}{\overset{\uparrow}{S}}-R' + Ph-\underset{NTs}{\underset{\downarrow}{S}}-C_6H_4-X\text{-}p \xrightarrow[\Delta]{Cu} R-\underset{NTs}{\underset{\downarrow}{\overset{O}{\overset{\uparrow}{S}}}}-R'$$

Sulfoxide		Sulfilimine	Sulfoximine
R	R'	X	Yield (%)[a]
Ph	Me	NO_2	65
Ph	Me	Cl	50
Ph	Me	H	63
Ph	Me	Me	40
Ph	Ph	NO_2	29
Ph	Tol-*p*	NO_2	24
Me	Me	NO_2	45
$—(CH_2)_4—$		NO_2	52
Ph	Me	NO_2	58
$[\alpha]_D^{25} = -122.5°$		$[\alpha]_D^{25} = +93.6°$	
(c = 3.23 acetone)		(c = 2.89 acetone)	

[a] Isolated yield.

shown earlier to react with tosylnitrene which was generated from tosyl azide to give the corresponding sulfide, but not the corresponding tosylsulfoximine,[9] in the presence of metallic copper the reaction gave the corresponding tosylsulfoximine in moderate yield.

The similar behavior between *N*-tosylsulfilimines and tosyl azide as the source of nitrene or nitrenoid–copper–complex seems to reflect on the formation of the deep green color at the initial step, which is probably due to the formation of a nitrenoid–copper–complex, or on that of the *N*-tosylsulfoximines, which are presumed to be formed by addition of "tosylnitrenoid" species formed from the sulfilimines to sulfoxides. This may be the first example of trapping the nitrene which was thermally generated from the *N*-sulfonylsulfilimine, whereas nitrenes which were photochemically generated from sulfilimines were reported to be trapped by olefins.[10,17] Thus, this is the first example of the use of the sulfilimine as an imino group transfer reagent for a useful synthesis of the *N*-tosylsulfoximines.

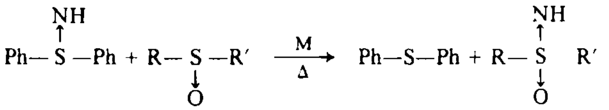
Reaction of N-Unsubstituted S,S-Diarylsulfilimines (5) with Sulfoxides

Treatment of *N*-unsubstituted diphenylsulfilimine (**5a**) with sulfoxides without solvent at 140°C, gives the corresponding *N*-unsubstituted sulfoximines in poor yields together with diphenyl sulfide. The use of copper powder increased slightly the yield of the sulfoximine at lower reaction temperatures, e.g. 130°C, although **5a** underwent hardly any decomposition at 130°C. The results of the reaction are shown in Table III.

The poor yields of the sulfoximines by this process are considered to be caused partly by the reaction of the thermally generated nitrene with the *N*-unsubstituted sulfoximines formed affording the reduction product, sulfoxides. Indeed, treatment

TABLE III

Reaction of *N*-unsubstituted sulfilimines with sulfoxides

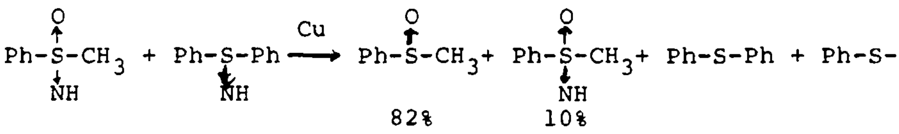


$$Ph-\overset{NH}{\overset{\uparrow}{S}}-Ph + R-\underset{O}{\underset{\downarrow}{S}}-R' \xrightarrow[\Delta]{M} Ph-S-Ph + R-\overset{NH}{\overset{\uparrow}{\underset{O}{\underset{\downarrow}{S}}}}\ R'$$

Sulfoxide					
R	R′	Temp (°C)	Time (min)	M	Yield (%)[a] Sulfoximine
Ph	Ph	140	15	—	4
Ph	Me	140	15	—	6
Me	Me	140	15	—	3
Ph	Ph	130	10	Cu	5
Ph	Me	130	10	Cu	15
Me	Me	130	10	Cu	8

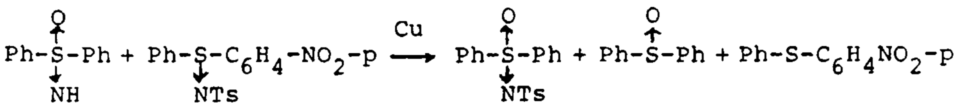
[a] Isolated yield.

of *N*-unsubstituted *S*-methyl-*S*-phenylsulfoximine with **5a** under the same condition gave methyl phenyl sulfoxide (82%) and the starting sulfoximine (10%), which is considered to be a mixture of the recovered one and that generated in the reaction of the reduced sulfoxide with the copper–nitrenoid–complex (Eq. (3))



$$Ph-\overset{O}{\overset{\uparrow}{\underset{NH}{\underset{\downarrow}{S}}}}-CH_3 + Ph-\underset{NH}{\underset{\downarrow}{S}}-Ph \xrightarrow{Cu} \underset{82\%}{Ph-\overset{O}{\overset{\uparrow}{S}}-CH_3} + \underset{10\%}{Ph-\overset{O}{\overset{\uparrow}{\underset{NH}{\underset{\downarrow}{S}}}}-CH_3} + Ph-S-Ph + Ph-S-CH_3 \quad (3)$$

In the same way, heating a mixture of *N*-unsubstituted diphenylsulfoximine with *S*-*p*-nitrophenyl-*S*-phenyl-*N*-tosylsulfilimine in the presence of copper gave the corresponding reduction product, diphenyl sulfoxide (70%) and diphenyl-*N*-tosylsulfoximine (15%) which is formed by the reaction of the sulfoxide with copper–nitrenoid–complex (Eq. (4))

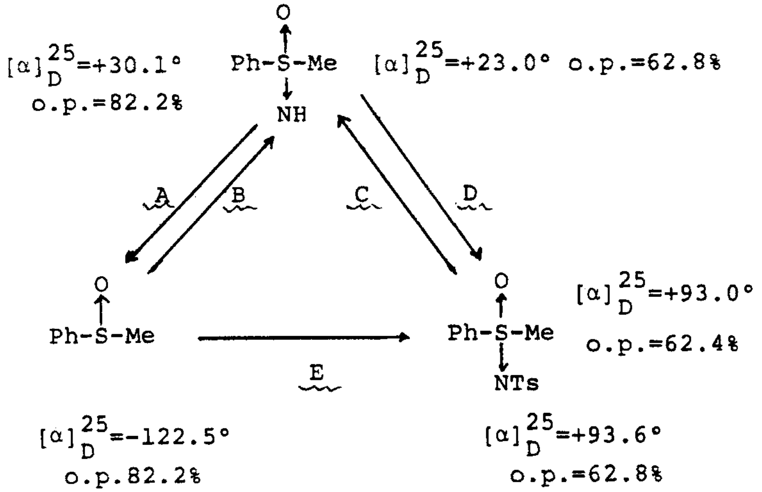


$$Ph-\overset{O}{\overset{\uparrow}{\underset{NH}{\underset{\downarrow}{S}}}}-Ph + Ph-\underset{NTs}{\underset{\downarrow}{S}}-C_6H_4-NO_2-p \xrightarrow{Cu} \underset{15\%}{Ph-\overset{O}{\overset{\uparrow}{\underset{NTs}{\underset{\downarrow}{S}}}}-Ph} + \underset{70\%}{Ph-\overset{O}{\overset{\uparrow}{S}}-Ph} + Ph-S-C_6H_4NO_2-p \quad (4)$$

Because of the poor yields, this system of using the *N*-unsubstituted sulfilimine as the imino group transfer agent may not be suitable for the preparation of the sulfoximines.

Stereochemistry

In order to examine the stereochemistry of the formation of *N*-tosylsulfoximines, *N*-unsubstituted (+)-(*S*)-*S*-methyl-*S*-phenylsulfoximine $[\alpha]_D^{25} = +30.1°$ (c 3.20 ace-



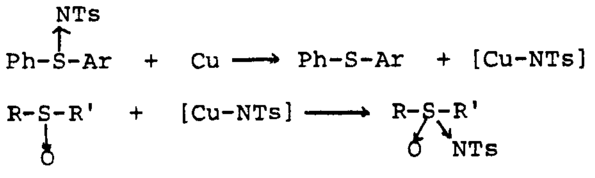
Path A: t-BuONO; B: HN_3-H_2SO_4; C: conc. H_2SO_4; D: TsCl/Py

E: Ph-$\underset{\text{NTs}}{\text{S}}$-$C_6H_4NO_2$-p - Cu

SCHEME 1 Reaction cycle.

tone), o.p. 82.2%, was prepared[18] and treated with *tert*-butyl nitrite in chloroform at 25°C to afford the (−)-(*S*)-methyl phenyl sulfoxide $[\alpha]_D^{25} = -122.5°$ (c 3.23 in acetone), o.p. 82.2%.[6] This optically active sulfoxide was then treated with a two-fold excess of *S*-*p*-nitrophenyl-*S*-phenyl-*N*-tosylsulfilimine in the presence of a 2-fold-excess of powdered copper at 190°C. *S*-Methyl-*S*-phenyl-*N*-tosylsulfoximine $[\alpha]_D^{25} = +93.6°$ (c 2.89 acetone) was separated carefully from the reaction mixture, in order to avoid further fractionation of the product. This sulfoximine was converted to the *N*-unsubstituted sulfoximine $[\alpha]_D^{25} = +23.0°$ (c 2.30 acetone), o.p. 62.8%, by treatment with concentrated sulfuric acid.[19,20]

This *N*-unsubstituted sulfoximine was allowed to react with tosylchloride in pyridine to afford the corresponding *N*-tosylsulfoximine $[\alpha]_D^{25} = +93.0°$ (c 2.18 acetone), o.p. 62.4%[4a] The results are summarized in Scheme 1. In this stereochemical cycle, the reactions (**A**, **B**, **C**, and **D**) in Scheme 1 are all known to proceed with retention of configuration around sulfur atom.[21–23] Consequently, the reaction to convert (−)-(*S*)-sulfoxide to (+)-*N*-tosylsulfoximine (path **E**) is known to proceed with retention (76% optical yield) of the configuration around the sulfur atom.



SCHEME 2

A partial racemization of the *N*-tosylsulfoximine thus formed is considered to be caused by thermal pyramidal inversion of the sulfoxide during the reaction.[24]

All the results described above suggest that the thermolyses of sulfilimines in the presence of copper are considered to proceed *via* an initial formation of the copper–nitrenoid–complex which is trapped with sulfoxides to give rise to the corresponding sulfoximines. The reaction is shown in Scheme 2.

EXPERIMENTAL

General. Melting points of the products were measured by Yanaco instrument and are uncorrected. IR spectra were obtained using a Hitachi 215 spectrophotometer. ^{1}H-NMR spectra of all the compounds were obtained with a Hitachi Perkin-Elmer R-20 spectrometer in 20% $CDCl_3$, using tetramethylsilane as an internal standard. Liquid chromatography was carried out by Yanaco-L-1030 instrument using methanol as an eluent. Thin layer chromatography was performed with Merck DC-Plastikfolien Kieselgel 60 F 254 F Art.5735 with fluorescent indicator, using various solvents and mixed solvents as eluents. Chloramine-T was obtained from Wako Pure Chemicals. Other chemicals were of reagent grade. Commercially available copper powder was used without further purification.

N-Tosylsulfilimines. All *N*-tosylsulfilimines were prepared from the corresponding sulfides and Chloramine-T by a modified Mann-Pope reaction.[25]

Sulfoxides. Dialkyl, alkyl aryl and diaryl sulfoxides, except dimethyl sulfoxide, were prepared by oxidation of the corresponding sulfides with sodium metaperiodate.[26] Commercial DMSO was dried (CaH_2) and purified by distillation.

N-Tosylsulfoximine. Either one of the following known methods **A** or **B** was used for the preparation of authentic samples of *N*-tosylsulfoximines

Method **A**. *S,S*-Diaryl- and *S*-methyl-*S*-phenyl-*N*-tosylsulfoximines were prepared by oxidation of the corresponding *N*-tosylsufilimines with sodium hypochlorite in EtOAc–H_2O two phase system.[8]

Method **B**. *S,S*-Dimethyl- and tetramethylenesulfoximines were prepared by treating the corresponding sulfoxides with tosyl azide in methanol in the presence of copper.[27]

Reaction of N-p-Tosylsulfilimines with Copper Powder. Typically, *S-p*-nitrophenyl-*S*-phenyl-*N*-tosylsulfilimine (1.0 g, 2.5 mmol) and copper powder (160 mg 2.5 mmol) were placed in a 30 ml round-bottomed-flask. The mixture was heated at 190°C for 10 min under N_2. The color of the reaction mixture turned to dark brown during the reaction. After the reaction, the flask was cooled with water, and the dark brown oily product was obtained. The reaction mixture was separated by column chromatography using benzene as an eluent. The products thus obtained were *p*-nitrophenyl phenyl sulfide (52 mg, 90%) and tosylamide (45 mg, 11%), which were identified by comparing their GLC behavior and IR and NMR spectra with those of authentic samples. Without copper, **3a** did not decompose even upon heating at 200°C for 24 h, affording the recovered sulfilimine quantitatively.

Similarly, *S*-methyl-*S*-phenyl-*N*-tosylsulfilimine afforded methyl phenyl sulfide (58%), diphenyl disulfide (12%), tosylamide (15%) and the recovered sulfilimine (16%).

Reaction of N-Unsubstituted Diarylsulfilimine with Copper. The reaction of *N*-unsubstituted *S,S*-diphenylsulfilimine (500 mg, 2.3 mmol) and copper (145 mg, 2.3 mmol) at 95°C for 30 min afforded diphenyl sulfide (420 mg quantitatively).

Reaction of S-p-Nitrophenyl-S-phenyl-N-tosylsulfilimine with Sulfoxide in the Presence of Copper. In a typical run, a mixture of the title sulfilimine (2.0 g, 5 mmol), diphenyl sulfoxide (500 mg, 2.5 mmol), and copper (315 mg, 5 mmol) was heated at 190°C for 1 h. Then the reaction mixture was cooled and poured into ice-water. The solution was extracted with benzene three times and then the organic layer was washed with water. The solvent was removed *in vacuo* after drying ($MgSO_4$). The products were separated by column chromatography using hexane and then benzene as eluents. The products thus obtained were diphenyl-*N*-tosylsulfoximine (266 mg, 29%) along with *p*-nitrophenyl phenyl sulfide, recovered diphenyl sulfoxide and reduced diphenyl sulfide. *N*-Tosylsulfoximines were identified by comparison (mp, IR and NMR spectra) with authentic samples. In the absence of copper, the original sulfilimine and sulfoxide were recovered in quantitative yields after the same treatment. Freshly precipitated copper powder is more suitable to let the reaction to proceed under mild conditions.

Preparation of N-Unsubstituted (+)-(S)-Methyl-phenylsulfoximine. This optically active sulfoximine was prepared by optical resolution of the racemic sulfoximine according to the method reported earlier.[18]

Preparation of (−)-(S)-Methyl Phenyl Sulfoxide. (+)-(*S*)-Methylphenylsulfoximine ($[\alpha]_D^{25} = +30.1°$, c = 3.20 in acetone, o.p. 82.2%) (3.0 g, 19.4 mmol) was dissolved in 20 ml of $CHCl_3$ at 25°C. To this solution was added a $CHCl_3$ solution (15 ml) of *tert*-butyl nitrite (2.0 g, 19.4 mmol) at 25°C. The solution was maintained for 20 min at 25°C. When evolution of gas ceased, the reaction was complete. After the solvent was removed under reduced pressure, the corresponding sulfoxide was obtained. Further purification was achieved by column chromatography. Methyl phenyl sulfoxide, $[\alpha]_D^{25} = -122.5°$, (c = 3.23, in acetone), o.p. 82.2%, was obtained in 97% yield.

Reaction of S,S-Diphenyl-N-tosylsulfilimine with Diphenyl Sulfoxide in the Absence of Copper. Sulfilimine (**3a**) (18 mg, 0.05 mmol) and diphenyl sulfoxide (10 mg, 0.05 mmol) were heated at 300°C for 30 min. The products thus obtained were diphenyl sulfide (87%), a trace amount of *N*-tosylsulfoximine and tosylamide (10%).

Reaction of (−)-(S)-Methyl Phenyl Sulfoxide with S-p-Nitrophenyl-S-phenyl-N-tosylsulfilimine in the Presence of Copper. (−)-(*S*)-Methyl phenyl sulfoxide ($[\alpha]_D^{25} = -122.5°$, c = 3.23 in acetone), (500 mg, 3.57 mmol), *S*-*p*-nitrophenyl-*S*-phenyl-*N*-tosylsulfilimine (2.8 g, 7.0 mmol) and copper powder (455 mg, 7.0 mmol) were heated at 190°C under N_2 for 1 h. After the reaction was complete, the reactor was cooled with water and the reaction mixture was separated by careful column chromatography using hexane and then benzene as eluents in order to avoid further fractionation of the product. *N*-Tosylsulfoximine, $[\alpha]_D^{25} = +93.6°$, (c = 2.89 in acetone) (640 mg) was obtained in 58% yield.

Conversion of (+)-(S)-Methyl-phenyl-N-tosylsulfoximine to N-Unsubstituted (+)-(S)-Sulfoximine. A mixture of (+)-(*S*)-*S*-methyl-*S*-phenyl-*N*-tosylsulfoximine ($[\alpha]_D^{25} = +93.6°$, c = 2.89 in acetone), (500 mg, 1.62 mmol) and 1 ml of concentrated H_2SO_4 was stirred for 15 min at 25°C. The resulting colorless solution was poured into 20 ml of water and made basic by adding sodium hydroxide solution below 25°C. The mixture was extracted with 10 ml portions of $CHCl_3$ three times. The combined extract was dried and evaporated under reduced pressure and the mixture was purified by column chromatography, using $CHCl_3$, as an eluent in order to avoid further fractionation of the product. *N*-Unsubstituted *S*-methyl-*S*-phenylsulfoximine ($[\alpha]_D^{25} = +23.0°$, c = 2.57 in acetone), (o.p. 62.8%) (243 mg) was obtained in 97% yield.

Conversion of N-Unsubstituted (+)-(S)-S-Methyl-S-phenylsulfoximine to (+)-(S)-S-Methyl-S-phenyl-N-tosylsulfoximine. (+)-(*S*)-*S*-Methyl-*S*-phenylsulfoximine ($[\alpha]_D^{25} = +23.0°$, c = 2.57 in acetone) (o.p. 62.8%), (200 mg, 1.3 mmol) was dissolved in 1 ml of dry pyridine. Tosylchloride (250 mg, 1.3 mmol) was then added to the above stirred solution and stirring was continued for 1 h at 25°C. The reaction mixture was poured into 10 ml of water and the solution was extracted with $CHCl_3$. The $CHCl_3$ solution was dried (silica gel) and the solvent was removed under reduced pressure to afford *N*-tosylsulfoximine, which was purified by column chromatography using benzene as an eluent in order to avoid further fractionation of the product. Yield was 367 mg (92%) $[\alpha]_D^{25} = +93.0°$, c = 2.18 in acetone, o.p. 62.4%.

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