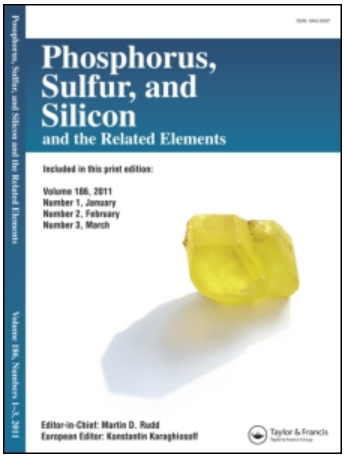


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# REDUCTIVE DEIMINATION OF SULFOXIMIDES AND SULFIMIDES WITH *P*-TOLUENESULFONYL NITRITE AND *T*-BUTYL THIONITRATE[1]

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# REDUCTIVE DEIMINATION OF SULFOXIMIDES AND SULFIMIDES WITH *P*-TOLUENESULFONYL NITRITE AND *T*-BUTYL THIONITRATE[1]

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Reduction of sulfimides and sulfoximides with *p*-toluenesulfonyl nitrite, a new nitrosating agent, gave nearly quantitatively the corresponding deimination products, sulfides and sulfoxides, respectively. In the reaction of dialkyl and aryl alkyl sulfoximides with *t*-butyl thionitrate, *N*-*t*-butylthiosulfoximides were obtained besides the usual deimination products, although diaryl sulfoximides were readily deiminated to the corresponding sulfoxides in good yields in the same treatment. *t*-Butyl thionitrate was also found to deiminate diphenyl sulfimide to give diphenyl sulfide in good yield. Sulfoximides reacted sluggishly with *t*-butyl thionitrite, however, eventually affording a small amount of sulfoxides.



In the course of studies on the synthetic application of thionitrite (R-SNO), thionitrate ($R\text{-}SNO_2$) and sulfonyl nitrite ($R\text{-}SO_2NO$),[2] we have shown that these three compounds are much better nitrosating reagents than alkyl nitrite and can be used in non-aqueous and neutral media. In particular, various aromatic amines were shown to undergo several deaminative substitutions such as halogenation,[3] arylation[3] and sulfenylation[4] to afford aromatic halides, biphenyls and aryl methyl sulfides, respectively, in excellent yields.

Earlier, Cram *et al.* reported that the deimination of sulfoximides, both with nitrosyl hexafluorophosphate ($NOPF_6$) in nitromethane and with nitrous acid ($HNO_2$) in aqueous media, gave in good yields the corresponding reduced sulfoxide possessing the same configuration as that of the original sulfoximide. In this reaction, the gas evolved from the reaction mixture was suggested as $N_2O$ without any experimental evidence.[5,6] These are excellent procedures for deiminative reduction of sulfoximides; however, the reagent, $NOPF_6$, is rather expensive and the reaction with $HNO_2$ has to be carried out in aqueous acidic media, which is inconvenient for acid-sensitive compounds. Another procedure for the deiminative reduction of diaryl sulfoximides is the treatment with elemental sulfur or diphenyl disulfide at 160°C, found by us.[7] This reaction, which gives corresponding sulfoxides quantitatively, however, is not suitable to reduce unsaturated compounds.

If, *t*-butyl thionitrate and *p*-toluenesulfonyl nitrite can be used for deiminative reduction, one can operate the reduction to remove the imino group from such compounds as sulfimides and sulfoximides under non-aqueous neutral reaction conditions. Indeed, we have found that both sulfoximides and sulfimides can be deiminated readily with these reagents. This paper deals with the deimination of various sulfoximides and sulfimides by treatment with both *p*-toluenesulfonyl nitrite and *t*-butyl thionitrate.

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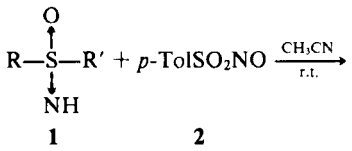
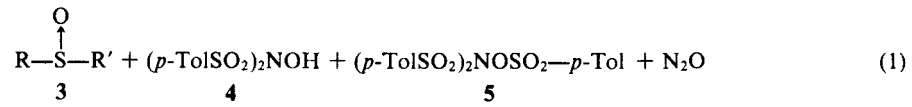
## RESULTS AND DISCUSSION

*Deimination with* p-*Toluenesulfonyl Nitrite:* When sulfoximide (**1**, 1.0 mmole) was treated with *p*-toluenesulfonyl nitrite (**2**, 3.0 mmole) in dry acetonitrile (5 ml) at room temperature under argon for ca 2h, the corresponding sulfoxide (**3**) was obtained nearly quantitatively, along with two side products (**4** and **5**) (Eq. 1). The deimination proceeded readily regardless of the structure of the sulfoximide, as shown in Table I. Although the deimination of dialkyl sulfoximide with nitrous acid has been known to yield dialkyl sulfone but not the sulfoxide,[8] both dimethyl and tetramethylene sulfoximides were found to be deiminated by *p*-toluenesulfonyl nitrite to afford the corresponding sulfoxides quantitatively. When the imino group is substituted, the sulfoximides, e.g. *N*-alkyl and *N*-tosyl sulfoximides are no longer deiminated at all with **2**. Although **3** and **5** of the products were isolated in pure state by column chromatography (silica gel, chloroform), it was difficult to isolate one of the side products, **4**, in the expected yield, since hydroxylamine **4** showed a long tailing in the chromatograph. The yield of **5** was ca 50–60% in mole % against **1** after purification and the ratio of **4** and **5** was nearly 1:2 in every case.



**1** **2**



**3** **4** **5** (1)

During the reaction, we observed an evolution of a gas which was determined to be $N_2O$ by conducting the reaction in a degassed anhydrous system and then analyzing the gas directly by mass spectrometry (m/e 44). Quantitative analysis was not carried out. NO gas(m/e 30) was also detected in the gaseous mass spectrum; however, it was considered to be formed by the partial decomposition of *p*-toluenesul-

TABLE I

Deimination of Sulfoximides with *p*-Toluenesulfonyl Nitrite at Room Temperature

| Sulfoximide R | R′ | | Reaction Time (h) | Solvent | Yield[a] (%) |
|---|---|---|---|---|---|
| $CH_3$ | $CH_3$ | **1a** | 2.0 | $CH_3CN$ | 100[b] |
| —$(CH_2)_4$— | | **1b** | 2.0 | $CH_3CN$ | 96 |
| $C_6H_5$ | $CH_3$ | **1c** | 2.0 | $CH_3CN$ | 94 (100[b]) |
| *p*-$CH_3O$—$C_6H_4$ | $CH_3$ | **1d** | 2.0 | $CDCl_3$ | 100[b] |
| *p*-$O_2N$—$C_6H_4$ | $CH_3$ | **1e** | 2.0 | $CDCl_3$—$CD_3CN$ | 100[b] |
| 2—$C_5H_4N$(Py) | $CH_3$ | **1f** | 2.0 | $CDCl_3$ | 100[b] |
| $C_6H_5$ | $C_6H_5$ | **1g** | 2.0 | $CH_3CN$ | 75 (85[c]) |
| *p*-$CH_3$—$C_6H_4$ | $C_6H_5$ | **1h** | 3.0 | $CH_3CN$ | 95 |
| *p*-Cl—$C_6H_4$ | $C_6H_5$ | **1i** | 3.0 | $CH_3CN$ | 98 |
| *p*-$O_2N$—$C_6H_4$ | $C_6H_5$ | **1j** | 3.0 | $CH_3CN$ | 89 |

[a] Isolated yield.
[b] Yield by NMR: no other product was detected.
[c] Yield by GLC.

fonyl nitrite, since NO gas was detected similarly in the control experiment in the absence of sulfoximide **1**.

The reaction (Eq. 1) required three equivalents of the reagent (**2**) to form the two side products, **4** and **5** as well as **3**. We consider that the reaction of **1** with **2** afforded at first **3** and *p*-toluenesulfinic acid (Eq. 2) which then reacted with excess **2**, eventually yielding **4** and **5**. Thus, we carried out the following control experiments (Eqs. 3 and 4). First, *p*-toluenesulfinic acid, freshly prepared by acidification of its sodium salt, was allowed to react immediately (the color of the brown sulfonyl nitrite **2** disappeared in several minutes) with an equivalent of **2** in dry acetonitrile under the same conditions, to afford **4** (68%, isolated) and a small amount of **5**, both of which were the only products observed by TLC (Eq. 3). Second, under similar conditions, **5** was obtained as the sole product by TLC in the reaction of freshly prepared **4** with an equivalent of **2** in ca 30 min, during which the color of **2** gradually diminished (Eq. 4).

$$\mathbf{1} + \mathbf{2} \longrightarrow \mathbf{3} + p\text{TolSO}_2\text{H} + \text{N}_2\text{O} \tag{2}$$

$$p\text{-TolSO}_2\text{H} + \mathbf{2} \xrightarrow{\text{fast}} \mathbf{4} + \mathbf{5} \tag{3}$$

$$\mathbf{4} + \mathbf{2} \xrightarrow{\text{slow}} \mathbf{5} \tag{4}$$

Thus, the reaction of Eq. 3 was faster than that of Eq. 4, and of course, faster than that of Eq. 2; therefore, *p*-toluenesulfinic acid formed at the initial stage of the reaction (Eq. 2) is consumed rapidly. This is in good accord with the absence of *p*-toluenesulfinic acid during the reaction. Consequently, the initial reaction of **1** and **2** should be nucleophilic attack of the nitrogen of **1** at the nitrogen of **2**. Although the effect of a polar substituent could not be adduced from the yield of substituted diphenyl sulfoxides (Table I) since the yields are all so excellent, we feel that the nucleophilic attack may not be very important in the rate-determining step.

Although no example of the deimination of a sulfimide with a nitrosating agent has been reported to date, diaryl sulfimides were also found to be deiminated by treatment with three equivalents of *p*-toluenesulfonyl nitrite to give the corresponding sulfides in good yields under the same conditions as in the deimination of sulfoximides (Eq. 5). Needless to say, *N*-tosyl sulfimide was not deiminated with **2**, as with *N*-alkyl and *N*-tosyl sulfoximides.

$$\text{R—S(NH)—R}' + \mathbf{2} \longrightarrow \text{R—S—R}' + \mathbf{4} + \mathbf{5}\ (+\text{N}_2\text{O}) \tag{5}$$

TABLE II

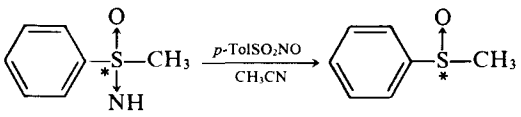
Deimination of Sulfimides with *p*-Toluenesulfonyl Nitrite at Room Temperature in Acetonitrile

| Sulfimide R | R′ | | Reaction Time (h) | Yield[a] (%) |
|---|---|---|---|---|
| $C_6H_5$ | $C_6H_5$ | **1a′** | 1.5 | 91 |
| *o*-$CH_3O$—$C_6H_4$ | $C_6H_5$ | **1b′** | 2.0 | 78 |
| *p*-$CH_3$—$C_6H_4$ | $C_6H_5$ | **1c′** | 2.0 | 54 |
| *p*-Cl—$C_6H_4$ | $C_6H_5$ | **1d′** | 1.5 | 76 |
| *p*-$O_2N$—$C_6H_4$ | $C_6H_5$ | **1e′** | 1.5 | 82[b] |

[a] Isolated yield.
[b] Yield by GLC.

These results are shown in Table II. The reaction is considered to proceed via the same mechanistic process as in the deimination of the sulfoximide.

*Stereochemistry:* When optically active methyl phenyl sulfoximide (**1c**) (R-(+), o.p. 95.9%) was treated similarly with three equivalents of *p*-toluenesulfonyl nitrite under the same conditions as above, the methyl phenyl sulfoxide (**3c**) (R-(−), o.p. 68.2%) which was obtained was found to retain 71% of the original configuration (Eq. 6). Since there is a possibility that the sulfoxide, formed during the reaction, underwent racemization in the reaction system, optically active methyl *p*-tolyl sulfoxide (**6**) (R-(+), o.p. 97.4%) was placed into the usual reaction system of dimethyl

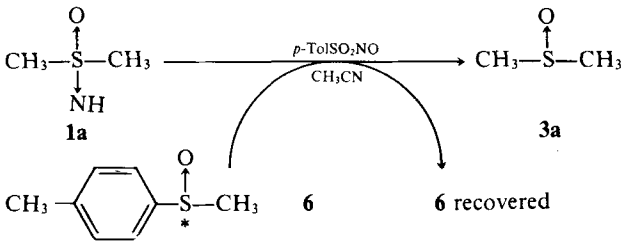



(6)

**1c** **3c**

$[\alpha]_D^{25}$ + 35.0° (c = acetone) o.p. 95.9% R—(+)

$[\alpha]_D^{25}$ − 101.6° (c = 1.00 in acetone) o.p. 68.2% R—(−)




(7)

**1a** **3a** **6** **6** recovered

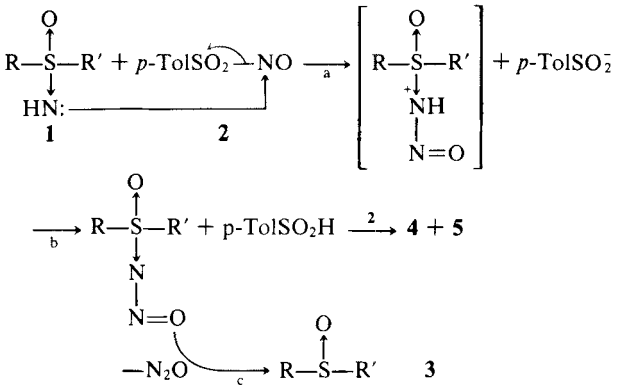
$[\alpha]_D^{25}$ + 144.3° (c = 1.12 in acetone) o.p. 97.4% R—(+)

$[\alpha]_D^{25}$ + 70.9° (c = 0.43 in acetone) o.p. 47.9% R—(+)

sulfoximide (0.54 mmole) with *p*-toluenesulfonyl nitrite (0.30 mmole) in dry $CH_3CN$ (5 ml). The methyl *p*-tolyl sulfoxide (o.p. 47.9%) recovered (72% yield) was found to be partially racemized (Eq. 7) (24.7% racemization). In addition, optically active methyl *p*-tolyl sulfoxide was found to racemize also upon mixing with either *p*-toluenesulfinic acid (14.3% racemization) or *p*-toluenesulfonyl nitrite (16.1% racemization) in $CH_3CN$ under the conditions employed for the deimination of the sulfoximide. Thus, the deimination of the sulfoximide with *p*-toluenesulfonyl nitrite is believed to have proceeded with nearly complete retention of configuration. The sulfoxide formed then would have undergone the well-known acid-catalyzed racemization involving oxygen exchange[9a] by *p*-toluenesulfinic acid formed during the reaction (Eq. 2) in the next step. In the initial stage of the deimination, some racemization would be taking place with *p*-toluenesulfonyl nitrite itself. However, it may be slow, since *p*-toluenesulfonyl nitrite can racemize even the sulfoxide and is much more abundant than *p*-toluenesulfinic acid which is rapidly consumed upon encounter with any excess nitrite. Nevertheless, the mechanism of racemization of sulfoxide with *p*-toluenesulfonyl nitrite is not clear. There is a possibility that the racemization may involve the formation of nitrosooxy sulfonium ion as was suggested earlier by us for the racemization of optically active sulfoxide with $N_2O_4$.[9b]

The deimination of the sulfoximide with *p*-toluenesulfonyl nitrite proceeded much more readily in a polar solvent such as acetonitrile or dimethyl sulfoxide than in a less polar solvent such as chloroform, as shown in Figure 1. This indicates the intervention of polar species in the rate-determining step.

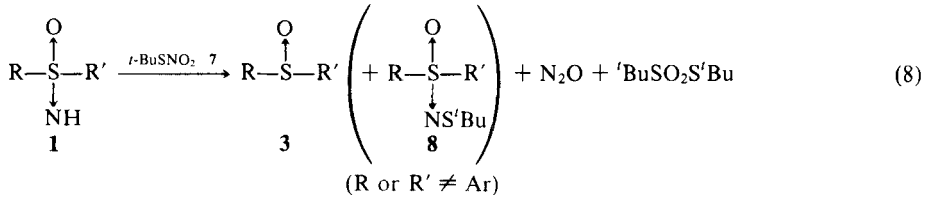
These results suggest that the deimination of sulfoximide with the sulfonyl nitrite involves the initial nitrosation of the imino group of the sulfoximide and subsequent extrusion of nitrous oxide, eventually yielding the corresponding sulfoxide, as shown in Scheme I.



Scheme I

At the same time, *p*-toluenesulfinic acid reacts with excess **2** to afford **4** and **5**. The absence of a clear-cut correlation between the reactivity and the polar effect of substituents seems to indicate that both processes of nucleophilic attack (a) and extrusion of $N_2O$(c) are involved in the rate-determining step, ultimately cancelling out the polar effect. The mechanism of the deimination of sulfimide seems to be nearly the same as that of sulfoximide.

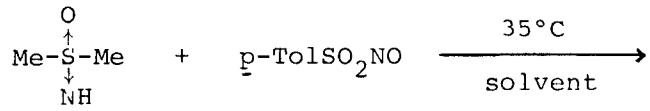
*Deimination with* t-*Butyl Thionitrate and* t-*Butyl Thionitrite:* The deimination of diaryl sulfoximides also proceeded with *t*-butyl thionitrate, an another nitrosating agent, readily affording the corresponding sulfoxides. When 1 mmole of sulfoximide (**1**) was treated in dry acetonitrile (5 ml) with 1.5 mmole of *t*-$BuSNO_2$ under argon atmosphere at room temperature, the corresponding sulfoxide (**3**) was obtained in good yield (Eq. 8, Table III).



(8)

(R or R′ ≠ Ar)

However, when both dialkyl and aryl alkyl sulfoximides were treated with **7**, *N*-*t*-butylthiosulfoximides (**8**) were obtained as side products along with the main by-product, $^tBuSO_2S^tBu$. Formation of *N*-*t*-butylthiosulfoximide (**8**) is considered to be due to the nucleophilic attack of sulfoximide on the sulfenyl sulfur atom of *t*-butyl thionitrate. This reaction is comparable to the reaction of alkylamines with *t*-butyl thionitrate which afforded alkyl sulfenamides.[10] Since the imino group of dialkyl



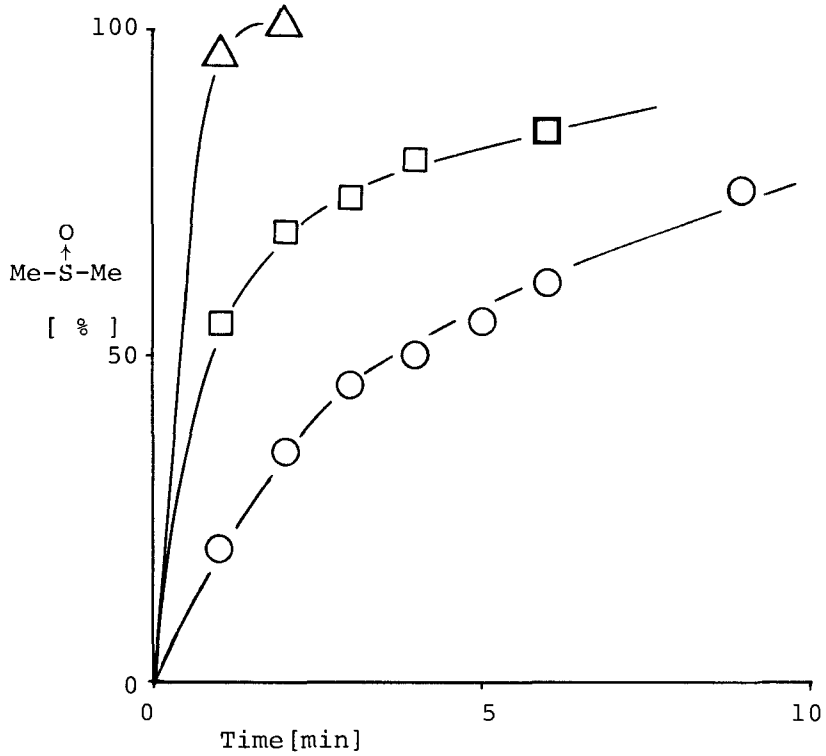




FIGURE 1 Solvent effect in the deimination of dimethyl sulfoximide with *p*-toluenesulfonyl nitrite at 35°C. ○: in $CDCl_3$; □: in $CD_3CN$; △: in $(CD_3)_2SO$.

sulfoximide or alkylamine should be a softer and better nucleophile as compared to that of diaryl sulfoximide or aromatic amine, their imino or amino group is considered to attack the soft sulfur atom of thionitrate rather than the nitrogen atom of the nitroso group. The gas evolved in the reaction was also determined to be $N_2O$ by mass spectrometry as with *p*-toluenesulfonyl nitrite.

Diphenyl sulfimide was also deiminated to diphenylsulfide in 80% yield upon treatment with *t*-butyl thionitrate. Thus, $^t$BuSNO$_2$ (**7**) was also confirmed to be a good deiminating agent for such compounds as diaryl sulfoximide and sulfimide. However, *t*-butyl thionitrite (*t*-BuSNO), which is another potent diazotizing agent,[2] was less effective for deimination; the corresponding sulfoxides were obtained in only 4–18% from sulfoximides (Table III). No *N*-sulfenylated product (*N*-*t*-butylthiosulfoximide) was obtained in the reaction with $^t$BuSNO, unlike the reaction with $^t$BuSNO$_2$. Both $^t$BuSNO$_2$ and $^t$BuSNO do not deiminate *N*-tosyl derivatives at all. When optically active methyl phenyl sulfoximide (**1c**) was also treated with *t*-butyl

TABLE III

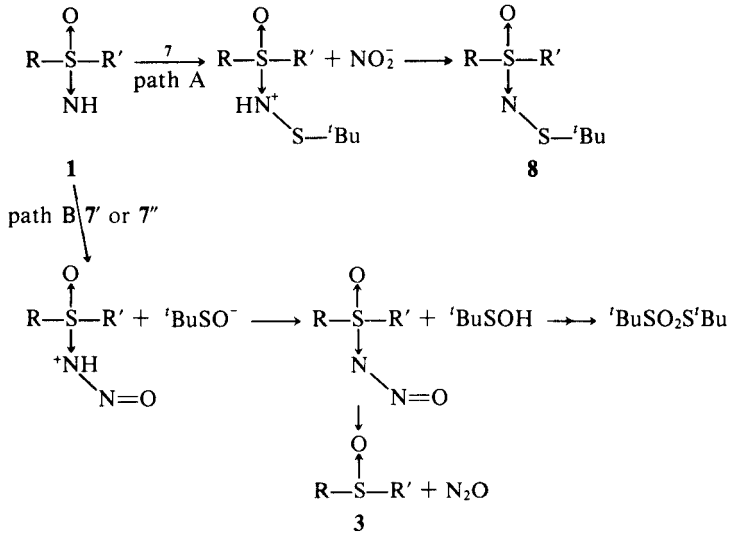
Deimination of Sulfoximides with *t*-Butyl Thionitrate and *t*-Butyl Thionitrite at Room Temperature in Acetonitrile

| Sulfoximide R | R′ | Reagent | Yield[a] 3 R—S(=O)—R′ | Yield[a] 7 R—S(=O)—N(↓)—S—*t*-Bu |
|---|---|---|---|---|
| $C_6H_5$ | $C_6H_5$ | *t*-$BuSNO_2$ | 71[b] | 0 |
| *p*-$CH_3$—$C_6H_4$ | $C_6H_5$ | *t*-$BuSNO_2$ | 85[b] | 0 |
| *p*-Cl—$C_6H_4$ | $C_6H_5$ | *t*-$BuSNO_2$ | 92[b] | 0 |
| *p*-$O_2N$—$C_6H_4$ | $C_6H_5$ | *t*-$BuSNO_2$ | 72[b] | 0 |
| $C_6H_5$ | $CH_3$ | *t*-$BuSNO_2$ | 52 | 14 **7a** |
| $CH_3$ | $CH_3$ | *t*-$BuSNO_2$ | 30 | 30 **7b** |
| $C_6H_5$ | $C_6H_5$ | *t*-BuSNO | 18[b] | 0 |
| $C_6H_5$ | $CH_3$ | *t*-BuSNO | 8 | 0 |
| $CH_3$ | $CH_3$ | *t*-BuSNO | 4 | 0 |

[a] Yield by NMR.
[b] Yield by GLC.



thionitrate, the corresponding sulfoxide (**3c**) that was obtained was found to retain 94% of the original configuration. The lack of racemization in this reaction is considered to be attributed to the non-formation of strong acid species or the rapid disappearance of acid species ($^t$BuSOH), in contrast to the reaction with the sulfonyl nitrite. Thus, the deimination of sulfoximide and sulfimide with *t*-butyl thionitrate **7** is presumed to proceed through the path shown in Scheme II.




Scheme II

*t*-Butyl thionitrate (**7**) is probably in equibrium with **7′** and also **7″** and the imino group of the sulfoximide may attack both the sulfur and nitrogen atoms, finally yielding both *N*-sulfenylated **8** and deiminated **3**. The absence of *N*-sulfenylated

product in the reaction of sulfoximide with $^t$BuSNO may indicate that the nucleophilic substitution on the sulfenyl sulfur of $^t$BuSNO with sulfoximide is very difficult mainly due to the low leaving-ability of the $NO^-$ group. $^t$BuSO$_2$S$^t$Bu formed in the reaction was confirmed by GLC and NMR spectra, and is considered to be derived from *t*-butyl sulfenate anion via the sulfenic acid or the sulfinyl radical.

The possibility of *N*-*t*-butylthiosulfoximide as an intermediate in the reaction with $^t$BuSNO$_2$ can be ruled out by the fact that *N*-*t*-butylthio- and *N*-*p*-tolylthiomethyl phenyl sulfoximides did not react at all with $^t$BuSNO$_2$ under the conditions used in this study. Therefore, the *N*-sulfenylated product from sulfoximide is only a side-product, as shown in Scheme II.

## EXPERIMENTAL

*General:* All melting points were taken on a Yanako instrument and were uncorrected. A Shimazu GC-6A instrument was used for gas chromatography using $N_2$ gas as a carrier gas. NMR spectra were taken on a Hitachi Perkin-Elmer R-20 spectrometer in $CDCl_3$ using TMS as an internal standard. IR spectra were recorded with a Hitachi 260-50 spectrometer. Optical rotations were measured at 25°C with a JASCO DIP-140 polarimeter. Mass spectra were taken with a Hitachi RMU-6MG mass spectrometer. Elemental analyses were carried out by the Chemical Analysis Center at this university.

t-*Butyl Thionitrite,* t-*Butyl Thionitrate and* p-*Toluenesulfonyl Nitrite:* The three title compounds were prepared by treating *t*-butyl mercaptan and *p*-toluenesulfinic acid with dinitrogen tetroxide, according to the methods reported earlier.[3b]

*Preparation of Sulfimides:* All free sulfimides were obtained by treating *N*-tosyl sulfimides, prepared by the reaction of sulfides with chloramine-T,[11] followed by treatment with concentrated sulfuric acid.[12] The mp of sulfimides are as follows: Diphenyl sulfimide(**1a'**), 74° (lit.[12] 74°). Phenyl *o*-methoxyphenyl sulfimide(**1b'**), 98–9° (lit.[13] 96–7°). Phenyl *p*-methylphenyl sulfimide(**1c'**), 51–2° (lit.[12] 48.5–50.5°). Phenyl *p*-chlorophenyl sulfimide(**1d'**), 46–7° (lit.[12] 48–9°). Phenyl *p*-nitrophenyl sulfimide(**1e'**), 107° (lit.[12] 98–9°).

*Preparation of Sulfoximides:* Sulfoximides were prepared by one of the following methods, A, B and C.

*Method A:* Aryl alkyl and dialkyl sulfoximides(**1a–1f**) were obtained by treating sulfoxides with sodium azide in the presence of concentrated sulfuric acid in chloroform.[14] Dimethyl sulfoximide(**1a**), mp 52° (lit.[15] 52–3°). Tetramethylene sulfoximide(**1b**), $bp_2$ 139–140° (bath temp.) (lit.[16] $bp_7$ 140°). Methyl phenyl sulfoximide(**1c**), $bp_3$ 141–2° (lit.[15] $bp_2$ 142–8°, mp 34–5°). Methyl *p*-nitrophenyl sulfoximide(**1e**), mp 148–9° (lit.[15] 147.5–8°). Methyl *p*-methoxyphenyl sulfoximide(**1d**), colorless crystals, mp 63–4°; NMR($CDCl_3$): $\delta$ 2.26 (b, 1H, NH), 3.06(s, 3H, $CH_3$), 3.85(s, 3H, $OCH_3$), 6.93(d, J = 8.3Hz, 2H, ArH), and 7.84(d, J = 8.3Hz, 2H, ArH); IR(KBr): 3250(=NH), 1220 & 1010cm$^{-1}$(O=S=N); Anal. Found: C, 51.95; H, 5.86; N, 5.71%, Calcd for $C_8H_{11}NO_2S$: C, 51.87; H, 5.98; N, 7.56%.

*Method B:* Methyl 2-pyridyl sulfoximide(**1g**) was prepared by direct oxidation of crude methyl 2-pyridyl sulfimide with MCPBA. The free sulfimide was obtained by treating with ammonia 2-pyridyl aminosulfonium salt formed in the reaction of the corresponding sulfide with MSH.[17] Mp 64–5° (lit.[17] 64.5–66°).

*Method C:* Sulfoximides(**1h–1k**) were prepared by oxidation of the corresponding free sulfimides with potassium permanganate in methanol or *t*-butanol.[12] Diphenyl sulfoximide(**1g**), mp 102° (lit.[15] 102–2.5°). Phenyl *p*-methylphenyl sulfoximide(**1h**), mp 103–4° (lit.[15] 101–2°). Phenyl *p*-chlorophenyl sulfoximide(**1i**), mp 94–5° (lit.[18] 95–6°). Phenyl *p*-nitrophenyl sulfoximide(**1j**), mp 160° (lit.[18] 159–9.5°).

*Deimination of Sulfoximides and Sulfimides with* p-*Toluenesulfonyl Nitrite:* A sulfoximide or sulfimide (1.0 mmole) dissolved in 5 ml of dry acetonitrile was added onto *p*-toluenesulfonyl nitrite (3.0 mmole). After stirring the mixture under argon for 1.5–3.0 h, the reaction mixture was poured into 1M aq. HCl solution and then extracted three times with chloroform (50 ml). The extract was washed with water and dried with $MgSO_4$. After solvent was removed under reduced pressure, the products including sulfoxide or sulfide, were separated and purified by subjecting the residue to silica gel column chromatography using chloroform or hexane as an eluent. All sulfoxides or sulfides obtained were identified by comparing the data of their GLC and IR with those of authentic samples. The side products, **4** and **5** were also separated in the same column chromatography and identified by comparison with reported data.[19,20]

*N,N-Bis*(p-*toluenesulfonyl*)*hydroxylamine* (**4**): Colorless crystals, mp 124–5° (lit.[19] 126°), NMR($CDCl_3$-$CD_3SOCD_3$): δ 2.39(s, 6H, $CH_3$), 7.10(d, J = 8.4Hz, 4H, ArH), 7.35(s, 1H, OH), and 7.56(d, J = 8.4Hz, 4H, ArH), IR(KBr): 3260(OH), 1375 and 1190($SO_2$) and 550$cm^{-1}$.

*N,N-Bis*(p-*toluenesulfonyl*)*amino* p-*toluenesulfonate*(**5**): Colorless crystals, mp 191° (lit.[20] 190–2°), NMR($CDCl_3$): δ 2.44(s, 9H, $CH_{33}$), 7.28(d, J = 8.5Hz, 4H, ArH), 7.35(d, J = 8.5Hz, 2H, ArH), 7.79(d, J = 8.5Hz, 4H, ArH), and 7.85(d, J = 8.5Hz, 2H, ArH).

Optically active sulfoximide was treated according to the same procedure as above. Optical purity of sulfoximide (95.9%) changed to 68.2% in sulfoxide, upon determination of the specific rotations (Eq. 6).

(+)-(*R*)-*Methyl phenyl sulfoximide:* Optically active title sulfoximide was prepared by optical resolution of the racemic sulfoximide(**1c**) with (+)-10-camphorsulfonic acid in acetone, according to the method reported by Johnson and Shroeck.[21]

*Solvent Effect:* Three equivalents of *p*-Tol$SO_2NO$(110 mg, 0.610 mmole) was added to a solution of dimethyl sulfoximide (18.9 mg, 0.203 mmole) in one of the three solvents($CDCl_3$, $CD_3CN$ and $CD_3SOCD_3$) (400 μl) in a NMR sample tube(d = 5φ), and then the spectrum was measured continuously. Changes of the integration of methyl signal of dimethyl sulfoxide produced were plotted at some intervals (see Figure 1).

*Reaction of* p-*Toluenesulfinic Acid with* p-*Toluenesulfonyl Nitrite:* To a solid mixture of **2** (200 mg, 1.08 mmole) and *p*-toluenesulfinic acid (168 mg, 1.08 mmole) dry $CH_3CN$ (5 ml) was added with a syringe under argon at room temperature. The color of **2** (light brown) disappeared within several minutes and the mixture was worked up by the same procedure as described in the deimination. TLC showed no other product except for **4** and **5**. **4** was isolated in 68% yield by column chromatography (silica gel, $CHCl_3$) and a trace of **5** was also isolated.

*Reaction of* ***4*** *with* p-*Toluenesulfonyl Nitrite:* A two-necked flask containing a solid mixture of ca 100 mg of **4** (0.29 mmole) and **2** (ca 50 mg, 0.27 mmole) was well-dried and flushed with argon. Dry $CH_3CN$ (3 ml) was added by syringe into the mixture at room temperature and the mixture was stirred for ca 30 min, while the color of **2** gradually faded. The resulting mixture showed only one spot on TLC. The product was determined as **5** by comparison with authentic sample.

*Racemization of Optically Active Methyl* p-*Tolyl Sulfoxide in The Reaction System of Dimethyl Sulfoximide with* p-*Toluenesulfonyl Nitrite:* In a 10 ml round-bottom flask were placed 50 mg of dimethyl sulfoximide, 50 mg of optically active methyl *p*-tolyl sulfoxide ($[\alpha]_D^{25}$ 144.3° (c = 1.12, acetone), o.p. 97.4%) and 300 mg of **2** under argon. To the solid mixture 5 ml of dry $CH_3CN$ was added and the mixture was stirred for ca 2 h. The resulting reaction mixture was poured into cold diluted NaOH solution and extracted three times with $CHCl_3$. The combined organic extract was washed with water and dried over anhydrous $MgSO_4$. The residue after removal of the solvent was subjected to the usual column chromatographical separation (silica gel, $CHCl_3$ as an eluent). The recovered and purified sulfoxide (21.5 mg) showed $[\alpha]_D^{25}$ 70.9° (c = 0.43, acetone) (o.p. 47.9%).

*Racemization of Optically Active Methyl* p-*Tolyl Sulfoxide by* p-*Toluenesulfonyl Nitrite and* p-*Toluenesulfinic Acid:* A mixture of 56 mg of the same sulfoxide as above and 50 mg of *p*-toluenesulfinic acid in 5 ml of dry $CH_3CN$ was stirred for 1.5 h under argon at room temperature. The sulfoxide obtained after the same work-up and purification had $[\alpha]_D^{25}$ 102° (c = 0.46, acetone) and 68.9% of optical purity. In the same treatment with *p*-toluenesulfonyl nitrite **2** (60 mg) instead of *p*-toluenesulfinic acid, the recovered sulfoxide showed $[\alpha]_D^{25}$ 96.5% (c = 0.44, acetone, o.p. 65.2%).

(+)-(*R*)-*Methyl* p-*tolyl sulfoxide* (**5**): Optically active title sulfoxide was obtained by the reaction of (+)-menthyl *p*-toluenesulfinate with the Grignard reagent of methyl iodide in ether, according to the method reported by Anderson.[22] Mp 74° (lit.[23] 73–4.5°).

*Deimination of Sulfoximides and Sulfimides with* t-*Butyl Thionitrate:* *t*-Butyl thionitrate (1.5 mmole) dissolved in 5 ml of dry acetonitrile was added on substrate (sulfoximide or sulfimide 1.0 mmole) under argon at room temperature. After stirring the mixture at room temperature for 2 h, the mixture was worked up by the same procedure as that used in the deimination with *p*-toluenesulfonyl nitrite.

In the case of sulfimide, reduced sulfide was isolated by column chromatography using benzene or hexane as an eluent on silica gel. Products in the reaction of sulfoximide, $^tBuSO_2S^tBu$, RS(O)($NS^tBu$)R′, RS(O)R′ and RS(O)(NH)R′ (recovery) were fractionated in that order by column chromatography (silica gel, $CHCl_3$ : EtOAc = 1 : 1).

Optically pure methyl phenyl sulfoximide ($[\alpha]_D^{25}$ 36.5° (c = 2.20 (acetone), o.p. 100%) was deiminated with *t*-$BuSNO_2$ by the procedure above to afford methyl phenyl sulfoxide ($[\alpha]_D^{25}$ −140.8°, c = 1.32 (acetone), o.p. 94%) which was obtained by column chromatography (silica gel, $CHCl_3$) after the usual work-up.

*Dimethyl* N-t-*butylthiosulfoximide* (***7a***): Colorless crystals, mp 98–9° (from ether); NMR ($CDCl_3$): δ 1.31(s, 9H, *t*Bu) and 3.10(s, 6H, $CH_3$); IR(KBr): 1180 & 1050$cm^{-1}$ (O=S=N); Anal. Found: C, 39.93; H, 8.40; N, 7.69%, Calcd for $C_6H_{15}NOS_2$: C, 39.74; H, 8.33; N, 7.72%.

*Methyl phenyl* N-t-*butylthiosulfoximide* (***7b***): Colorless crystals, mp 49–50° (from benzene-hexane); NMR($CDCl_3$): δ 1.30(s, 9H, *t*-Bu), 3.15(s, 3H, $CH_3$) and 7.43–7.97(m, 5H, ArH); IR(KBr): 1200, 1090 & 980 $cm^{-1}$ (O=S=N); Anal. Found: C, 54.23; H, 7.03; N, 5.76%, Calcd for $C_{11}H_{17}NOS_2$: C, 54.28; H, 7.04; N, 5.75%.

*Deimination of Sulfoximide with* t-*Butyl Thionitrite:* A mixture of sulfoximide (ca 0.5 mmole) and *t*-butyl thionitrite (ca 0.7 mmole) in dry $CH_3CN$ was stirred for 10 h at room temperature. After the usual work-up, the yield of sulfoxide was determined by GLC or NMR (See Table III). In this case, no *N*-*t*-butylthiosulfoximide was obtained.

*Determination of Gas Evolved in The Deimination of Sulfoximide with* p-*Toluenesulfonyl Nitrite or* t-*Butyl Thionitrate:*[24] A mixture of *p*-toluenesulfonyl nitrite (3.0 mmole) or *t*-butyl thionitrate (1.5 mmole) in dry acetonitrile (10 ml) was placed in a two-necked flask which was attached to a vacuum line. The mixture was frozen by cooling with liq. nitrogen and degassed three times using a diffusion pump. After solid diphenyl sulfoximide (1.0 mmole) was added from a bent tube, the mixture was stirred for 5 h at room temperature. The gas evolved was pumped into the gas sampler by a Toepler pump. The gas obtained was introduced into the mass spectrometer for identification. m/e 44($N_2O$), m/e 30(NO).



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