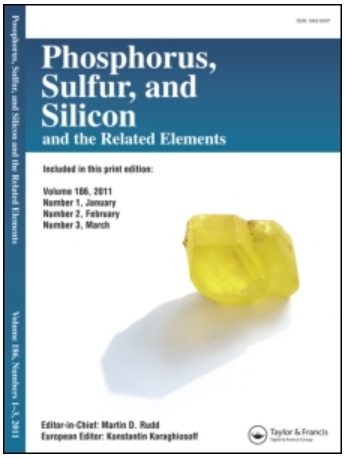

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Akutagawa, Kunihiko , Furukawa, Naomichi and Oae, Shigeru(1984) 'A FACILE CONVERSION OF SULFOXIMINES AND SULFONEDIIMINES TO SULFOXIDES AND SULFILIMINES WITH *TERT*-BUTYL NITRITE', Phosphorus, Sulfur, and Silicon and the Related Elements, 19: 3, 369 — 374
To link to this Article: DOI: 10.1080/03086648408077601
URL: http://dx.doi.org/10.1080/03086648408077601

Phosphorus and Sulfur, 1984, Vol. 19, pp. 369–374
0308-664X/84/1903-0369/$18.50/0

A FACILE CONVERSION OF SULFOXIMINES AND SULFONEDIIMINES TO SULFOXIDES AND SULFILIMINES WITH *TERT*-BUTYL NITRITE

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(*Received September 23, 1983; in final form January 12, 1984*)

N-Unsubstituted sulfoximines and *N*-mono-tosylsulfonediimines were found to react readily with *tert*-butyl nitrite to give the corresponding sulfoxides and *N*-tosylsulfilimines in high yields with no racemization.

Interest in the chemistry of the aza analogues[1] of sulfone such as sulfoximines[2] and sulfonediimines[3] has increased within the past ten years. However, their chemical reactivities have not been fully explored as yet except for a few scattered utilizations in organic syntheses, e.g. such as an alkylidene-transfer reagent.[4] There are now several reliable methods for preparing sulfoximines (**1**) and sulfonediimines (**2**) and their *N*-substituted derivatives. Recently, sodium hypochlorite and chloramine-*T* have been found to be excellent oxidizing reagents for sulfilimines to sulfoximines.[5-7] However, less attention has been paid to the reduction of sulfoximines (**1**) or sulfonediimines (**2**) to sulfoxides or sulfilimines. Several procedures for the deiminative reduction of sulfoximines (**1**) have been found through treatment with such sulfur compounds as elemental sulfur,[8] disulfide,[9] and sulfenyl chloride,[10] or with nitrosating reagents such as nitrous acid in aqueous acidic media,[11] nitrosyl hexafluorophosphate ($NOPF_6$) in nitromethane,[12] *tert*-butyl thionitrate and tosylnitrite.[13] In these interconversions, it is desirable that the reactions should proceed not only with stereoselectivity but also afford the desired products in high yields. The reaction of sulfoximines with such sulfur compounds as diphenyl disulfide affords the corresponding sulfoxides in good yields with partial racemization. The reactions however, cannot be applied to sulfoximines that have functional groups, e.g. an olefin linkage which is sensitive to the deiminative reductant such as disulfide. In the reductions with well-known nitrosating reagents, i.e. nitrous acid in aqueous acidic media, $NOPF_6$ in nitromethane, *tert*-butyl thionitrate and tosylnitrite in acetonitrile, partial racemization of the products has often been observed.[13,14] These reactions generally require excess of the nitrosating reagents. In an attempt to convert sulfoximines (**1**) and sulfonediimines (**2**) to the corresponding sulfoxides and *N*-tosylsulfilimines, treatment of *N*-unsubstituted sulfoximines and *N*-mono-tosylsulfonediimines with *tert*-butyl nitrite was found to afford readily the corresponding

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sulfoxides and *N*-tosylsulfilimines in nearly quantitative yields under neutral mild reaction conditions.

This paper deals with this general procedure for the mild reductive deimination of sulfoximines and sulfonediimines with *tert*-butyl nitrite.

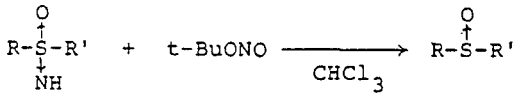
RESULTS AND DISCUSSION

The reagent that was successfully employed for this reductive deimination is readily available *tert*-butyl nitrite. The conversion of *N*-unsubstituted sulfoximines (**1**) and *N*-monotosylsulfonediimines (**2**) to sulfoxides and *N*-tosylsulfilimines with *tert*-butyl nitrite proceeded smoothly in chloroform or dichloromethane at 25°C within 10 min. The work-up procedure is very simple, involving only removal of the solvent and of *tert*-butyl alcohol formed in the reaction, and affords the corresponding deiminative derivatives in nearly pure form without any further purification. The results obtained from various **1** and **2** are shown in Tables I and II.

Although the deiminating reaction of dialkyl sulfoximines with nitrous acid in acidic media under various reaction conditions was reported to give dialkyl sulfones,[15] but not the sulfoxides, the reactions of *N*-unsubstituted-**1** and *N*-monotosyl-**2** with

TABLE I

Reductive deimination of sulfoximines with *t*-BuONO



(1)

R	R′	Solvent	Reaction time (min)	Yield (%)[a]
Ph	Ph	$CHCl_3$	10	99
Ph	Ph	CH_2Cl_2	20	98
Ph	C_6H_4—Cl-*p*	$CHCl_3$	10	100
Ph	C_6H_4—NO_2-*p*	$CHCl_3$	15	100
Ph	C_6H_4—CH_3-*p*	$CHCl_3$	10	99
Ph	C_6H_4—OCH_3-*p*	$CHCl_3$	15	97
Ph	CH_3	$CHCl_3$	10	100
Ph	CH_3	$CDCl_3$	15	100[b]
p-CH_3—C_6H_4	CH_3	$CHCl_3$	15	98
p-CH_3O—C_6H_4	CH_3	$CHCl_3$	15	96
—$(CH_2)_4$—		$CHCl_3$	10	100
CH_3	CH_3	$CHCl_3$	10	100
Ph	CH_3	$CHCl_3$	10	100

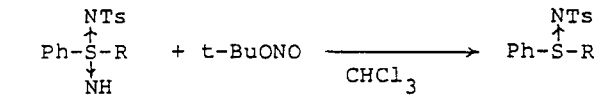
:$[\alpha]_D^{25} = +30.1°$ (c = 3.60, in acetone), o.p. = 82.2%

:$[\alpha]_D^{25} = -122.5°$ (c = 2.70, in acetone), o.p. = 82.2%

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

TABLE II

Reductive deiminations of sulfonediimines with *t*-BuONO



(2)

R	Solvent	Reaction time (min)	Yield (%)[a]
Ph	$CHCl_3$	10	100
Ph	CH_2Cl_2	30	100
C_6H_4—Cl-*p*	$CHCl_3$	20	100
C_6H_4—NO_2-*p*	$CHCl_3$	20	100
C_6H_4—CH_3-*p*	$CHCl_3$	20	99
C_6H_4—OCH_3-*o*	$CHCl_3$	30	100
CH_3	$CHCl_3$	10	99
CH_3	$CDCl_3$	15	100[b]

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

tert-butyl nitrite gave no side product but solely the corresponding sulfoxides and *N*-tosylsulfilimines in quantitative yields.

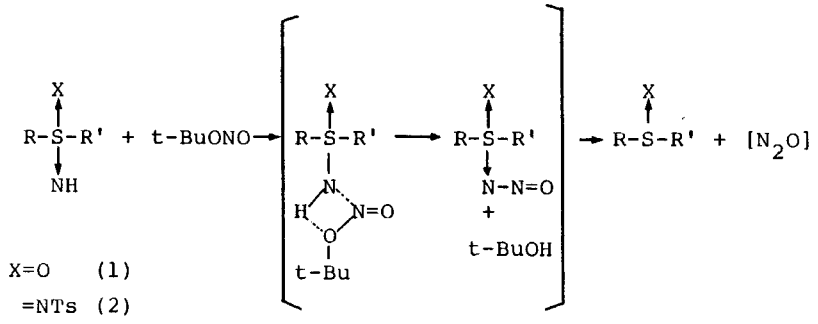
In order to explore the stereochemistry of the formation of the sulfoxide, (+)-(*S*) methyl phenyl sulfoximine, $[\alpha]_D^{25} = +30.1°$ (c 3.60 in acetone), o.p. 82.2%, was prepared according to a known method[16] and treated under similar reaction condition. Methyl phenyl sulfoxide, $[\alpha]_D^{25} = -122.5°$ (c 2.70, in acetone), o.p. 82.2%, was obtained quantitatively in this reaction, implying that this reaction proceeds with retention (100%) of configuration around the sulfur atom.

This method has the following characteristic features:

(1) All kinds of *N*-unsubstituted sulfoximines (**1**) and *N*-monotosylsulfonediimines (**2**) can be simply and cleanly converted to the corresponding sulfoxides and *N*-tosylsulfilimines, respectively with an equimolar amount of inexpensive and readily available nitrosating reagent (*t*-BuONO) under mild reaction conditions. The products, i.e. sulfoxides and *N*-tosylsulfilimines did not react at all with *tert*-butyl nitrite.

(2) The deimination proceeds with complete retention of configuration around the sulfur atom under neutral and mild reaction conditions. Thus, the procedure to convert sulfoximine to sulfoxide provides a convenient process for the preparation of optically active sulfoxides hitherto unavailable except by the reaction of menthyloxysulfinates with Grignard reagents.[17] Racemic sulfoxide can be readily converted in good yields, by treatment with hydrazoic acid[18] or *O*-mesitylenesulfonylhydroxylamine (MSH)[19] to sulfoximines which in turn are basic enough to be resolvable as salts of optically active sulfonic acids.[16] Finally, optically active sulfoximines can be converted stereospecifically to optically active sulfoxides by this reductive deimination.

(3) Sulfoximines and sulfonediimines that have substituents on the imino group, e.g. *N*-alkyl-, *N*-acyl-, *N*-sulfonylsulfoximines did not react at all with *tert*-butyl nitrite. The *N*-tosylsulfilimines formed from *N*-mono-tosyl-sulfonediimines were not deiminated further with *tert*-butyl nitrite.



SCHEME 1 Reductive deimination of sulfoximines and sulfonediimines with *t*-butyl nitrite.

In this reductive deimination of sulfoximines and sulfonediimines with *tert*-butyl nitrite, the *N*-nitrososulfoximine is considered to be an important intermediate in the reduction,[13] but was not isolated during the reaction. The hetero atom bearing one or more lone pairs, combined with the imino nitrogen of sulfoximines, obviously weakens the central *S(VI)-N* linkage to result in the facile fission of the *S-N* linkage affording the corresponding sulfoxide.[20] Evidence to support this hypothesis arises from the fact that these types of sulfoximines and sulfonediimines are nearly unknown, whereas *N*-chloro-, *N*-sulfenyl-, and *N*-sulfinylsulfoximines, which also possess *α*-hetero atoms bearing lone pairs attached to the imino nitrogen readily decompose thermally yielding the corresponding sulfoxide.[10] The *N*-nitrososulfoximine which has an extremely good leaving group, N_2O, may be readily decomposed to give the corresponding sulfoxide. The whole scheme for the reaction is shown in Scheme 1.

EXPERIMENTAL

General. Melting points of the products were measured by a Yanaco instrument and are uncorrected. Ir spectra were taken on a Hitachi 215 spectrophotometer. Nmr spectra of all compounds were taken with a Hitachi Perkin-Elmer R-20 spectrometer in $CDCl_3$ using TMS as an internal standard. Thin layer chromatographs were taken with Merck DC-Plastiko-folien Kieselgel 60 F 254 Art.5735 with fluorescent indicator, using chloroform, benzene or mixed solvents as the eluent. Optical rotations were measured at 25 °C with a JASCO DIP-140 polarimeter. *tert*-Butyl nitrite was obtained from Wako Pure Chemicals. Chloroform and dichloromethane were purified by the usual procedures.

Preparation of Sulfoximines. One of the following methods **A** and **B** available for preparation of sulfoximine was selected.

Method A. Diarylsulfoximines (**1**) were prepared by oxidation of the corresponding *N*-unsubstituted sulfilimines with sodium hypochlorite in aqueous methanol under alkaline conditions.[5] Diphenyl-**1**, m.p. 102.5–103.0 °C (lit.,[5] 103.0 °C). *p*-Chlorophenylphenyl-**1**, m.p. 95.5–96.0 °C (lit.,[5] 95.5–96.0 °C). *p*-Nitrophenylphenyl-**1**, m.p. 159.0–159.5 °C (lit.,[5] 159.0–159.5 °C). *p*-Tolylphenyl-**1**, m.p. 102.0–102.5 °C (lit.,[5] 102.5–102.5 °C). *o*-Methoxyphenylphenyl-**1**, m.p. 160.0–161.0 °C (lit.,[5] 160.0–161.0 °C).

Method B. Other sulfoximines except diaryl derivatives were obtained by treating the corresponding sulfoxides with sodium azide in the presence of concentrated sulfuric acid in chloroform.[18] Methylphenyl-**1**, m.p. 34.0–35.0 °C (lit.,[21] 34–35 °C). Methyl-*p*-tolyl-**1**, m.p. 71.0–72.0 °C (lit.,[21] 71–72 °C), *p*-Methoxyphenylmethyl-**1**, m.p. 63.0–63.5 °C (lit.,[13] 63–64 °C). Tetramethylene-**1**, b.p. 123.0–124.0 °C/2.5 mmHg (lit.,[22] 140 °C/7 mmHg). Dimethyl-**1**, m.p. 51.5–52.5 °C (lit.,[21] 52–53 °C).

Preparation of (+)-(S) methyl-phenylsulfoximine. This sulfoximine was prepared by optical resolution of the racemic sulfoximine, which was prepared by the method described above, with (+)-10-camphorsulfonic acid in acetone, according to the method reported earlier.[16]

Preparation of sulfonediimines. Sulfonediimines (**2**) were prepared by treating the corresponding *N*-unsubstituted sulfilimines with chloramine-*T* in the presence of excess sodium salt of tosylamide in anhydrous acetonitrile.[7] Diphenyl-*N*-monotosyl-**2**, m.p. 153.0–153.5 °C (lit.,[7] 153.0–153.5 °C). *p*-Chlorophenylphenyl-**2**, m.p. 124.0 °C (lit.,[7] 124.0–124.5 °C). *p*-Nitrophenylphenyl-**2**, m.p. 154.5–155.0 °C (lit.,[7] 154.5–155.0 °C). Phenyl-*p*-tolyl-**2**, m.p. 128.0–129.0 °C (lit.,[7] 128.0–129.0 °C). *o*-Methoxylphenylphenyl-**2**, m.p. 171.0–172.0 °C (lit.,[7] 171.0–172.0 °C). Methylphenyl-**2**, m.p. 162.0–163.0 °C (lit.,[7] 162.0–163.0 °C).

Reactions of sulfoximines and sulfonediimines with tert-butyl nitrite. A sulfoximine or *N*-tosylsulfonediimine (1.0 mmol) was dissolved in 5 ml of chloroform at 25 °C. To this solution was added the chloroform solution (2 ml) of *tert*-butyl nitrite (1.0 mmol) at 25 °C. The solution was maintained for 10 min at 25 °C. After evolution of gas stopped the reaction was complete. When the solvent and *tert*-butyl alcohol thus obtained were removed under reduced pressure, the corresponding sulfoxide or *N*-tosylsulfilimine was obtained in pure form. The structure was identified by comparing the data of their TLC, HPLC, and IR with those of authentic samples. Optically active methylphenylsulfoximine, $[\alpha]_D^{25} = +30.1°$ (c 3.60 in acetone), o.p. 82.2%, was also treated similarly with *tert*-butyl nitrite to afford the corresponding sulfoxide, $[\alpha]_D^{25} = -122.5°$ (c 2.70 in acetone), o.p. 82.2%, according to the same procedure as described above.

Reduction in NMR tube. NMR spectrum of the substrate, methylphenylsulfoximine or *N*-tosylsulfonediimine (0.1–0.3 mmol), was measured in $CDCl_3$. To the solution in an NMR sample tube an equimolar amount of *tert*-butyl nitrite was added at 25 °C. After the reaction completed, NMR spectra of the resulting mixtures were taken and TLC and HPLC of the reaction mixture were also measured. The products thus obtained were the corresponding sulfoxide or *N*-tosylsulfilimine and *tert*-butyl alcohol.

Reaction of diphenyl-N-tosylsulfilimine with tert-butyl nitrite. Diphenyl-*N*-tosylsulfilimine (1.0 mmol) was dissolved in chloroform (5 ml) which was then added to a chloroform (2 ml) solution of *tert*-butyl nitrite (1.0 mmol). After stirring the mixture for 1 h, the solution was removed under reduced pressure and the *N*-tosylsulfilimine was recovered in 100% yield.

Reaction of diphenyl-N-methyl- and N-tosylsulfoximines with tert-butyl nitrite. Treatment of the title sulfoximines with *tert*-butyl nitrite under the same condition as described above afforded no reductive product and the title compounds were recovered quantitatively.

Reaction of optically active methyl phenyl sulfoxide with tert-butyl nitrite. One equivalent of *tert*-butyl nitrite (1 mmol) in chloroform (5 ml) was added to a solution of methyl phenyl sulfoxide, $[\alpha]_D^{25} = -122.5°$ (c 2.26 in acetone), op. 82.2% (1 mmol), in chloroform (5 ml). After stirring the mixture for 15 min, the solvent was removed under reduced pressure. Methyl phenyl sulfoxide was recovered quantitatively without racemization.

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