

A CONVENIENT PREPARATION OF N-(ARENESULFONYL) SULFOXIMINES  
BY OXIDATION OF N-(ARENESULFONYL) SULFILIMINES WITH SODIUM  
HYPOCHLORITE IN A TWO PHASE SYSTEM

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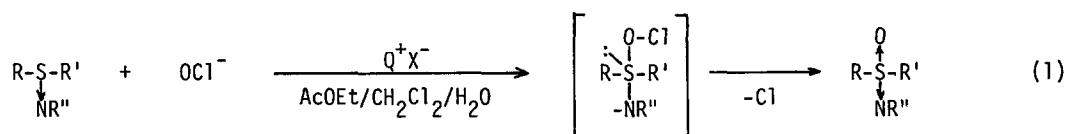
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SUMMARY : *N*-(Arenesulfonyl)sulfilimines can be oxidized to the corresponding  
sulfoximines in high yields with sodium hypochlorite in an AcOEt-H<sub>2</sub>O  
two phase system in the presence of quaternary ammonium salts as catalysts.

Sulfoximines are attractive organic sulfur compounds as alkylidene or chiral transfer reagent like sulfur ylides.<sup>1)</sup> For example, Johnson et al. revealed that  $\alpha$ -sodio derivatives of *N*-(arenesulfonyl)sulfoximines are useful nucleophilic alkylidene transfer reagents, e.g., for the conversion of aldehydes and ketones to the corresponding oxiranes.<sup>2)</sup> As to synthetic procedures for *N*-(arenesulfonyl)sulfoximines following several methods have been exploited, namely, oxidations of sulfilimines,<sup>3)</sup> oxidative iminations of sulfoxides,<sup>2,4)</sup> formations of sulfur-carbon linkages of sulfoximines<sup>5)</sup> and sulfonylations of *N*-H sulfoximines.<sup>6)</sup> However, except for sulfonylation of *N*-H sulfoximines, these methods have only limited uses to prepare *N*-sulfonyl *S,S*-dialkyl and *S*-alkyl *S*-aryl sulfoximines. Only the other route to prepare *S,S*-diaryl *N*-(arenesulfonyl)sulfoximines involves treating arenesulfonylchlorides with the corresponding *N*-H sulfoximines which are prepared by oxidation of *N*-H sulfilimines<sup>6)</sup> with potassium permanganate,<sup>7)</sup> sodium metaperiodate<sup>8)</sup> or *m*-chloroperbenzoic acid,<sup>6)</sup> however this procedure needs several steps. Recently, Swern<sup>9)</sup> and Johnson<sup>3)</sup> reported that oxidation of *S,S*-diphenyl *N*-(*p*-tolylsulfonyl)sulfilimine with *m*-chloroperbenzoate anion or perhydroxy anion generated *in situ* in basic aqueous alcoholic media affords the corresponding sulfoximine

in high yield. However, Johnson described that *N*-(arenesulfonyl)sulfilimines were not successfully oxidized by sodium hypochlorite anion.<sup>3)</sup> We have found however, treatment of *N*-sulfonyl sulfilimines with sodium hypochlorite can afford corresponding oxidized sulfoximines by selecting appropriate solvents and catalysts in a two-phase reaction system.

In this communication, we report a convenient and general method to prepare *N*-(arenesulfonyl)sulfoximines using hypochlorite anion in a phase transfer catalyzed system consisting of 10% aqueous sodium hypochlorite-ethyl acetate at room temperature in the presence of a quaternary ammonium salt.



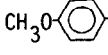








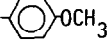







The oxidation is achieved by mixing aqueous sodium hypochlorite solution to vigorously stirred system of *N*-(arenesulfonyl)sulfilimine and a quaternary ammonium salt in a mixed solvent of ethyl acetate-methylene chloride. All the sulfilimines were consumed within a few hours. A typical experimental procedure is as follows: to a solution of *S,S*-diphenyl *N*-(*p*-tolylsulfonyl) sulfilimine (1.0 g, 2.8 mmol) and tetrabutylammonium bromide (0.40 g, 1.2 mmol) in 20 ml of ethyl acetate, was added a two fold excess of sodium hypochlorite solution (4.2 g). The mixture was vigorously stirred at room temperature and the reaction was monitored by HPLC or TLC. After usual work-up processes, the products thus obtained were identified by comparison of their IR and NMR spectra and mp with those of authentic materials. The results obtained are shown in the Table.

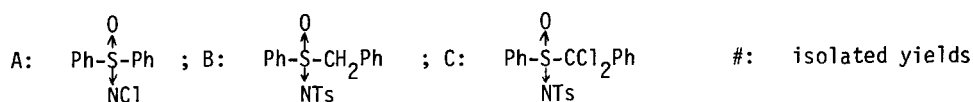
Inspection of the results reveals the following characteristic features. i) All kinds of *N*-substituted sulfilimines can be converted to the corresponding sulfoximines in high yields with the present reaction system. ii) Interestingly, we observed that the oxidation of this kind depends remarkably on both catalyst and solvent used. Quaternary ammonium salts such as *n*-Bu<sub>4</sub>NBr, *n*-Bu<sub>4</sub>NCl, *n*-Bu<sub>4</sub>NHSO<sub>4</sub> and CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>NMe<sub>3</sub>Br catalyze the reaction, however, generally accepted phase transfer catalysts such as PhCH<sub>2</sub>NEt<sub>3</sub>Cl, 15-crown-5, 18-crown-6 and dibenzo-18-crown-6 did not catalyze the oxidation. Ethyl acetate and acetonitrile are excellent solvents but other ordinary solvents such as methanol, tetrahydrofuran and dioxane are ineffective. iii) Sulfoxides and sulfur ylides also react with sodium hypochlorite to give the corresponding

TABLE Preparation of N-(arenesulfonyl)sulfoximines



R	R'	R''	Yield(%) <sup>#</sup>	QX	R	R'	R''	Yield(%) <sup>#</sup>	QX
Ph	Ph	Ts	98	a					
Ph	Ph	Ts	100	b	Ph	CH <sub>3</sub>	-SO <sub>2</sub> - 	85	a
Ph	Ph	Ts	35	c	Ph	CH <sub>3</sub>	-SO <sub>2</sub> -Ph	90	a
Ph	Ph	Ts	43	d		CH <sub>3</sub>	Ts	82	a
Ph	Ph	Ts	100	e		CH <sub>3</sub>	Ts	80	a
Ph	Ph	Ts	8	f		CH <sub>3</sub>	Ts	86	a
Ph	Ph	Ts	5	g					
Ph	Ph	Ts	trace	h	Ph	Et	Ts	90	a
Ph	Ph	Ts	trace	i	Ph		Ts	71	a
Ph	Ph	Ts	trace	j			Ts	80	a
Ph	Ph	Ts	trace	k					
Ph		Ts	93	a	Ph		Ts	78	a
Ph		Ts	93	a	Ph		Ts	73	a
Ph		Ts	90	a	Ph		-SO <sub>2</sub> - 	70	a
Ph		Ts	94	a		-(CH <sub>2</sub> ) <sub>4</sub> -	Ts	77	a
Ph		Ts	90	a		-(CH <sub>2</sub> ) <sub>5</sub> -	Ts	74	a
					CH <sub>3</sub>	CH <sub>3</sub>	Ts	12	a
					CH <sub>3</sub>	CH <sub>3</sub>	Ts	83	d
Ph		Ts	95	a	Ph	Ph	Cl	92	a(A)
Ph	CH <sub>3</sub>	Ts	92	a	Ph	Ph	H	95	a(A)
					Ph	-CH <sub>2</sub> -Ph	Ts	10(B), 61(C)	a

a: n-Bu<sub>4</sub>NBr; b: n-Bu<sub>4</sub>NCl; c: n-Bu<sub>4</sub>NClO<sub>4</sub>; d: n-Bu<sub>4</sub>NHSO<sub>4</sub>; e: CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>NMe<sub>3</sub>Br; f: PhCH<sub>2</sub>NEt<sub>3</sub>Cl;  
g: CH<sub>12</sub>H<sub>25</sub>NMe<sub>3</sub>Cl; h: 18-crown-6; j: 15-crown-5; k: non



sulfones and sulfur oxydides under the same condition, however treatment of sulfides, e.g., diphenyl sulfide, did not give corresponding sulfoxide nor sulfone. iv) Sodium hypochlorite is also known to be a chlorinating reagent. Therefore, under the condition indicated in the Table S-benzyl S-phenyl N-(p-tolylsulfonyl)sulfoximine once formed is immediately chlorinated at the S- $\alpha$ -benzylic carbon affording eventually  $\alpha,\alpha$ -dichlorosulfoximine. In fact, the sulfoximine obtained by oxidation of S-benzyl derivative with m-chloroperbenzoic acid in methylene chloride was also chlorinated at S- $\alpha$ -benzylic carbon under the same condition.

These observations suggest clearly that this oxidation involves an initial nucleophilic addition of hypochlorite anion on the N-(arenesulfonyl)sulfinimidoyl sulfur to form an incipient intermediate sulfurane, and subsequent elimination of chloride anion as shown in the eq. 1. Since both N-(arenesulfonyl)sulfilimines<sup>10)</sup> and sodium hypochlorite are readily in access, this reaction is an excellent alternative and general method for synthesis of N-(arenesulfonyl)-sulfoximines.

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(Received in Japan 19 June 1981)