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Oxidation of *N*-(*p*-Tolylsulfonyl)sulfilimines to *N*-(*p*-Tolylsulfonyl)sulfoximines with Alkaline Hydrogen Peroxide

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The anions derived from *N*-(*p*-tolylsulfonyl)sulfoximines are of considerable synthetic utility as alkylidene transfer reagents for the conversion of aldehyde and ketones into oxiranes.[1] Routes to *N*-tosylsulfoximines include treatment of the corresponding NH sulfoximine with *p*-toluenesulfonyl chloride, the copper-catalyzed reaction of sulfoxides with *p*-toluenesulfonyl azide,[1,2] and the oxidation of *N*-(*p*-tolylsulfonyl)sulfilimines.[3] These latter compounds are themselves readily available from the reaction of sulfides with Chloramine-T.[4,5] *N*-(Arylsulfonyl)-*S*,*S*-dimethylsulfoximines are available by copper-catalyzed reactions of Chloramine-T and related compounds with dimethyl sulfoxide.[1,6]

The oxidation of *N*-(*p*-tolylsulfonyl)sulfilimines to the corresponding sulfoximines has generally been carried out with aqueous potassium permanganate.[3,4] One literature report describes the use of the sodium salt of *m*-chloroperoxybenzoic acid to effect this oxidation.[7] Recently, Swern reported on the high yield oxidation of *N*-acyl- and *N*-(arylsulfonyl)dimethylsulfilimines to the corresponding sulfoximines with ruthenium tetroxide; the reaction may be accomplished with catalytic amounts of ruthenium tetroxide if sodium metaperiodate or sodium hypochlorite is added to the reaction mixture.[8]

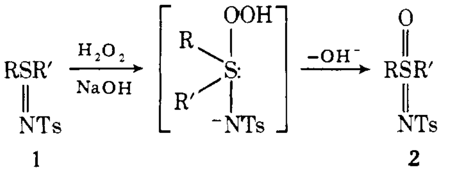
We would like to report here our finding that *N*-(*p*-tolylsulfonyl)sulfilimines (**1**) are readily oxidized in good yield to *N*-(*p*-tolylsulfonyl)sulfoximines (**2**) with alkaline hydrogen peroxide. These oxidations are achieved by adding 2 equiv of sodium hydroxide and hydrogen peroxide in water to a refluxing solution of the *N*-(*p*-tolylsulfonyl)sulfilimine in methanol. The mixture is allowed to reflux for 2 h and then worked up by pouring into water and extracting the *N*-(*p*-tolylsulfonyl)sulfoximine with chloroform. In some instances, the *N*-(*p*-tolylsulfonyl)sulfoximine crystallizes from the reaction mixture in pure form on cooling. This oxidation procedure is applicable to a variety of *N*-(*p*-tolylsulfonyl)sulfilimines as shown in Table I.

Table I. Preparation of *N*-(*p*-Tolylsulfonyl)sulfoximines

sulfoximine **2**		yield,	mp,	lit.[a] mp,
R	R′	%	°C	°C
Ph	CH_3	98	107–109	107–109
Ph	C_2H_5	88	123–125	
Ph	*i*-C_3H_7	80	98.5–99.5	
Ph	c-C_5H_9	44	142–143	142.5–143.5
Ph	c-C_6H_{11}	65	145–147	145.5–146
Ph	CH_2Ph	29	151–152	148–149
CH_3	CH_3	78	169–179	169–170
C_2H_5	C_2H_5	88	93–94	89–91
n-C_4H_9	*n*-C_4H_9	60	57–58	

[a] Reference 1.

The success of these oxidation reactions with nucleophilic oxidants can be attributed to the highly electonegative *N*-tosyl substituent, which increases the electrophilic character of the sulfilimine sulfur. We suggest that these oxidants proceed via an intermediate sulfurane (eq 1). Results with two other inexpensive nucleophilic oxidants, sodium hypochlorite and *tert*-butyl hydroperoxide/base, have not been satisfactory.[9]



(1)

Experimental Section

***S*,*S*-Diethyl-*N*-(*p*-tolysulfonyl)sulfoximine.** *S*,*S*-Diethyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2.31 g, 0.01 mol) was dissolved in 30 mL of refluxing methanol. A solution of 0.8 g [0.02 mol of sodium hydroxide and 2.1 mL of 30% hydrogen peroxide (~0.02 mol)] in 8 mL of water was added. The mixture after stirring and refluxing for 5 h was poured into 75 mL of water and extracted twice with 30-mL portions of chloroform. The combined chloroform extracts were washed with 20 mL of water, dried over $MgSO_4$, and evaporated. The residue was recrystallized from ethanol to yield 2.4 g (88%) of product, mp 93–94 °C.

Registry No.—1(R = Ph; R′ = CH_3), 10330-22-0; **1** (R = Ph; R′ = C_2H_5), 10330-18-4; **1** (R = Ph; R′ = *i*-C_3H_7), 18922-56-0; **1** (R = Ph; R′ = c-C_5H_9), 69765-76-0; **1** (R = Ph; R′ = c-C_6H_{11}), 56561-39-8; **1** (R = Ph; R′ = CH_2Ph), 24702-30-5; **1** (R = CH_3; R′ = CH_3), 13150-75-9; **1** (R = C_2H_5; R′ = C_2H_5), 13553-69-0; **1** (R = *n*-C_4H_9; R′ = *n*-C_4H_9), 17627-00-8; **2** (R = Ph; R′ = CH_3), 42153-74-2; **2** (R = Ph; R′ = C_2H_5), 69765-77-1; **2** (R = Ph; R′ = *i*-C_3H_7), 69780-68-3; **2** (R = Ph; R′ = c-C_5H_9), 33332-99-9; **2** (R = Ph; R′ = c-C_6H_{11}), 33367-88-3; **2** (R = Ph; R′ = CH_2Ph), 38764-59-9; **2** (R = CH_3; R = CH_3), 22236-45-9; **2** (R = C_2H_5; R′ = C_2H_5), 42153-72-0; **2** (R = *n*C_4H_9, R′ = *n*-C_4H_9), 69765-78-2; H_2O_2, 7722-84-1.

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Diels–Alder Reactions of 2*H*-Thiopyran

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During the course of our investigation of functionalized cyclic dienes, we have examined the Diels–Alder reaction of 2*H*-thiopyran (**1**).[1] Our original thinking led us to predict that 2*H*-thiopyran would be a relatively reactive diene because of the electron-donating character of sulfur and further that the sulfur atom could be used to control regioselectivity. We also predicted that the Alder endo effect would lead to products having the same carbon skeleton stereochemistry as expected

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