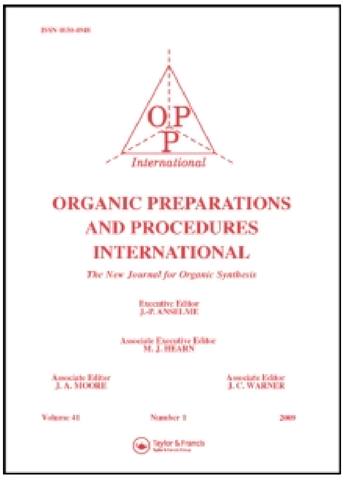

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SYNTHESIS OF OPTICALLY ACTIVE N-(p-TOLUENESULFONYL)-SULFOXIMINE BY SULFOXIDE AND CHLORAMINE T - COPPER[1]

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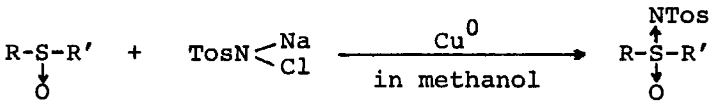
Although optically active aralkyl sulfoximines have been synthesized,[2,3] no optically active dialkyl and diaryl sulfoximine has been prepared except methionine sulfoximine.[4] Carr *et al*. prepared dimethyl-N-(*p*-toluenesulfonyl)sulfoximine in 80% yield by the copper-catalyzed reaction of chloramine-T with DMSO.[5] We have synthesized three optically active sulfoximines from the corresponding optically active sulfoxides, with chloramine T - copper system in methanol, as shown in the Table.



$$R\text{-}\underset{\overset{\downarrow}{O}}{S}\text{-}R' \quad + \quad TosN{<}^{Na}_{Cl} \xrightarrow[\text{in methanol}]{Cu^0} R\text{-}\overset{\overset{NTos}{\uparrow}}{\underset{\overset{\downarrow}{O}}{S}}\text{-}R'$$

(+)-(R)-(I) (-)-(R)-(II)

Although the yield shown in the Table are not high, the percentage of conversion are nearly quantitative based on the amount of unreacted sulfoxides recovered.

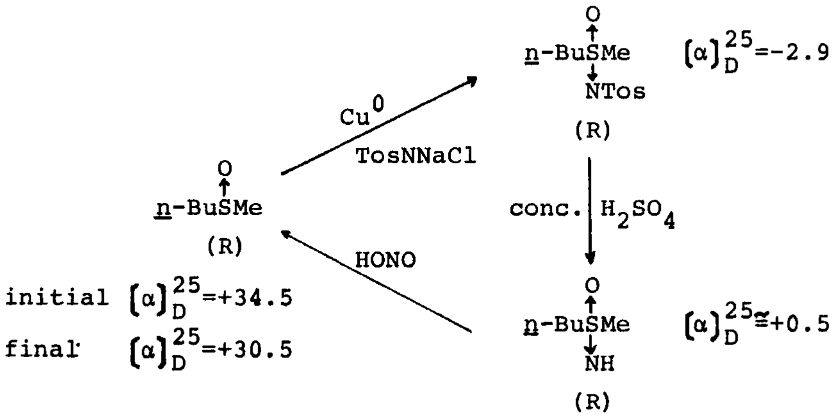
When a mixture of chloramine-T and cupric salt ($CuCl_2$, $CuSO_4$ and $Cu(acac)_2$) was used, the yields of the sulfoximines are very poor (below 5%) while the optical activity remained the same.

Table. N-(p-Toluenesulfonyl)sulfoximines[a]

	Substrate(I)			Product(II)[b]	
	R	R′	$[\alpha]_D^{25}$	Yield(%)	$[\alpha]_D^{25}$
a:	n-Bu	Me	+34.5	37(55)	-2.9(-3.0)
b:	p-Tol	Me	+143	40(58)	-131 (-136)
c:	p-Tol	Ph	+22.0	25(31)	-13 (-14)

a) Chloroform was used in specific rotation measurement.
b) Results with tosyl azide are shown in parentheses.

In order to correlate the skeletal configuration of the sulfoximine (IIa) obtained, it was converted to the original sulfoxide by hydrolysis with concentrated sulfuric acid and subsequent deimidation with nitrous acid. The complete reaction cycle is shown below.



The result clearly demonstrates the reaction occurred with net retention and to be as useful for the synthesis of optically active sulfoximines as the reaction with tosyl azide-copper reagent system.

EXPERIMENTAL

Optically active n-butyl methyl sulfoxide (Ia), methyl p-tolyl sulfoxide (Ib) and phenyl p-tolyl sulfoxide (Ic) were prepared by the method of Andersen.[6]

Optically Active N-(p-Toluenesulfonyl)sulfoximines (II).- A methanol solution (10 ml) containing the sulfoxide (3 mmol), chloramine-T (or tosyl azide) (4 mmol) and copper powder (0.004 g-atom) was refluxed with stirring for 4 hr. After filtration of the hot solution, the solvent was evaporated to give a green oil. It was extracted with chloroform and the solution was shaken with a saturated Na_2EDTA solution, then with water, and dried. After removal of the chloroform, the residue was chromatographed through a column packed with silica gel, using chloroform as eluent. The ir and nmr spectra of these sulfoximines thus obtained were identical to those of the racemic authentic samples.[7] (IIa) and (IIb) were crystallized from ethanol and acetone, respectively. (IIa): mp 63-64.5°, (IIb): mp 161-162°, (IIc): colorless oil. $[\alpha]_D^{25}$ Values and yields are listed in the Table.

Hydrolysis of (-)-Sulfoximine (IIa) to (+)-Free Sulfoximine.- A concentrated sulfuric acid solution (2 ml) containing the sulfoximine (2 mmol) was stirred for 1 hr at room temperature. The resulting clear colorless solution was poured into 50 ml of cold water and made basic by addition of solid sodium carbonate. The mixture was extracted three times each with 50 ml of chloroform. The combined extracts were dried, filtered and evaporated under reduced pressure. The light yellow oil obtained gave ir and nmr spectra identical to those of authentic sample.[7] The yield was 80%; $[\alpha]_D^{25} \sim +0.5$ (c = 1.5 in $CHCl_3$).

Conversion of (+)-Free Sulfoximine to (+)-Sulfoxide (Ia).-The free sulfoximine (1.6 mmol) was dissolved in 7 ml of 2N sulfuric acid, into which sodium nitrite (3.2 mmol) was added. After the solution was stirred at room temperature for 1 hr, it was made alkaline by addition of solid sodium carbonate. The mixture was extracted a few times each with 10 ml of chloroform. The combined extracts were dried, filtered and evaporated under reduced pressure. The ir and nmr spectra of the oil obtained was identical to those of the starting sulfoxide. The yield was 87%; $[\alpha]_D^{25}$ +30.5 (c = 1.03 in $CHCl_3$).

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