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Asymmetric Oxidation of Benzyl *p*-Tolyl Sulfide with Active Halogeno Compounds in the Presence of Optically-Active Alcohols

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Synopsis. The oxidation of benzyl *p*-tolyl sulfide with active halogeno compounds such as *N*-bromosuccinimide, *N*-chlorosuccinimide and *t*-butyl hypochlorite, affords optically-active benzyl *p*-tolyl sulfoxide. The absolute configuration of the sulfoxide obtained depends on the chirality of the alcohols used.

In previous papers,[1,2] the authors have reported that *N*-bromo-ε-caprolactam (NBC) or *N*-chloro-nylon-66 (NCN-66) oxidizes sulfides to the corresponding sulfoxides in the presence of water or alcohols. During the course of the study of the oxidation, a novel asymmetric induction was found in the presence of optically-active alcohols.[3,4] But the dependence of the absolute configuration of the sulfoxides on the chirality of alcohols used is different for NBC and for NCN-66. Accordingly, in the present note, the asymmetric oxidation of benzyl *p*-tolyl sulfide (I) with various other reagents in the presence of optically-active alcohols is reported.

Experimental

The chemical reagents and procedure are essentially the same as those described previously.[3]

The assignments of the reaction products were performed on the basis of NMR and IR spectra and elemental analysis.

The optical purity of the benzyl *p*-tolyl sulfoxide obtained was calculated from published data: (*R*)-(+)-benzyl *p*-tolyl sulfoxide, $[\alpha]_D$ +252° (acetone).[5]

Results and Discussion

Optically-active benzyl *p*-tolyl sulfoxide was formed by all the active halogeno compounds used in the presence of optically-active alcohols.

In the case of alcohols listed in Table 1, the absolute configuration of I obtained depends on the chirality of the alcohols used.

It is generally assumed that the oxidation of sulfides with active halogeno compounds in the presnece of alcohols results in the formation of alkoxysulfonium salts.[6] And the alkoxysulfonium salts can either form sulfoxides by the elimination of alkyl halides, followed by the retention of the configuration at the sulfur atom,[7] or yield sulfoxides by hydrolysis, followed by an inversion of the configuration.[8]

Thus, the oxidation of I with NBC in the presence of an (*R*)-alcohol forms more of the (*S*)-alkoxysulfonium salt than the (*R*)-alkoxysulfonium salt, and the hydrolysis of a mixture of the salts leads to larger amounts of the corresponding (*R*)-sulfoxide than that of the (*S*)-sulfoxide.

In the case of other oxidation reagents, the predominantly formed (*S*)-alkoxysulfonium salt leads to the corresponding (*S*)-sulfoxide with the elimination of an alkyl halide.

On the other hand, the results using (−)-menthol as the alcohol differ from those described above. As shown in Table 2, the oxidation of I with *N*-halogeno compounds in the presence of (−)-menthol preferentially produces the corresponding (*R*)-sulfoxide, but the oxidation of I with *t*-butyl hypochlorite gives the (*S*)-sulfoxide dominantly. Accordingly, the mechanism for the oxidation of I with *t*-butyl hypochlorite differs from that for the oxidation with *N*-halogeno compounds.

On the basis of these results, it is postulated that the

TABLE 1. ASYMMETRIC OXIDATION OF BENZYL *p*-TOLYL SULFIDE WITH ACTIVE HALOGENO COMPOUNDS IN THE PRESENCE OF OPTICALLY-ACTIVE ALCOHOLS AT −20 °C

Halogeno compound	Alcohol	Solvent	Time (h)	Sulfoxide Yield (%)	$[\alpha]_D$[e] (°)	Opt. yield (%)	Abs. config.
NBC[a]	(*R*)-(−)-2-Octanol	CH_2Cl_2	70	28.0	+1.21	0.48	R
	(*S*)-(+)-2-Octanol	CH_2Cl_2	72	67.4	−0.31	0.12	S
NCN-66[b]	(*R*)-(−)-2-Octanol	Toluene	20	15.4	−2.65	1.05	S
	(*S*)-(+)-2-Octanol	Toluene	20	16.6	+2.98	1.22	R
NCS[c]	(*R*)-(−)-2-Octanol	CH_2Cl_2	20	9.6	−26.18	10.41	S
	(*R*)-(−)-2-Octanol	Toluene	20	8.7	−5.88	2.33	S
	(*S*)-(+)-2-Octanol	CH_2Cl_2	20	14.3	+13.06	5.18	R
	(*S*)-(+)-2-Octanol	Toluene	20	27.9	+0.98	0.39	R
t-BuOCl[d]	(*R*)-(−)-2-Octanol	Toluene	10	14.0	−1.45	0.58	S
	(*S*)-(+)-2-Octanol	Toluene	10	16.2	+1.06	0.42	R
	(*R*)-(−)-Borneol	Toluene	10	5.3	−0.73	0.29	S

a) *N*-Bromo-ε-caprolactam. b) *N*-Chloro-nylon-66. c) *N*-Chlorosuccinimide. d) *t*-Butyl hypochlorite. e) Determined in acetone.

Table 2. Asymmetric oxidation of benzyl *p*-tolyl sulfide in the presence of (*R*)-(−)-menthol at −20 °C

Halogeno compound	Solvent	Time (h)	Sulfoxide Yield (%)	Sulfoxide $[\alpha]_D$[c] (°)	Sulfoxide Opt. yield (%)	Sulfoxide Abs. config.
NBC	CH_2Cl_2[a]	70	47.0	+1.90	0.80	R
	CH_2Cl_2[b]	70	10.6	+0.42	0.17	R
	Toluene[a]	70	5.0	+102.00	41.00	R
	Toluene[b]	70	5.2	+1.43	0.57	R
NCN-66	Toluene[b]	20	20.9	+2.10	0.83	R
NBS	Toluene[b]	20	1.4	+7.57	3.00	R
NCS	Toluene[b]	20	4.6	+1.16	0.46	R
t-BuOCl	Toluene[b]	10	37.6	−2.24	0.89	S

a) Kept at −78 °C before the addition of (*R*)-(−)-menthol. b) Kept at −20 °C before the addition of (*R*)-(−)-menthol. c) Determined in acetone.

oxidation of sulfides with active halogeno compounds in the presence of potically-active alcohols affords the corresponding optically-active sulfoxides. The absolute configuration of the sulfoxides obtained depends on the chirality of the alcohols used, and the oxidation reagents affect the route of oxidation of the sulfides.

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