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ASYMMETRIC OXIDATION OF SULFIDES TO SULFOXIDES BY N-BROMO-ε-CAPROLACTAM IN THE PRESENCE OF OPTICALLY ACTIVE ALCOHOLS

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Oxidation of sulfides with N-bromo-ε-caprolactam in the presence of optically active alcohols affords the corresponding optically active sulfoxides. The absolute configuration of the sulfoxides obtained depends on the chirality of the alcohols used. The stereochemical course of this asymmetric oxidation is discussed.

Recently, we have found that N-bromo-ε-caprolactam (NBC) is a good oxidant of sulfides to sulfoxides,[1)] like a number of N-halogen compounds such as N-chloro-[2)] and N-bromosuccinimides,[3)] 1-chlorobenzotriazole,[4)] and N-chloro nylon 66.[5)] During the course of the study of the oxidation with NBC,[6)] we have now found a novel asymmetric induction in oxidation. Namely, when alkyl aryl sulfides were oxidized partially (sulfoxide yields; less than 50%) with NBC at low temperature, the corresponding optically active sulfoxides were obtained.

A typical partial oxidation of benzyl p-tolyl sulfide is described below. A solution of 1.92 g(10 mmol) of NBC in 50 ml of carbon tetrachloride was treated dropwise with a solution of 2.14 g(10 mmol) of benzyl p-tolyl sulfide in 100 ml of carbon tetrachloride at -20 ∿ -30°C. After 1 hr stirring, (R)-(-)-menthol ($[\alpha]_D$ -49.5°(EtOH))(20 mmol) was added. And then the reaction mixture was allowed to stand for 70 hr at -20°C followed by washing with an aqueous sodium hyposulfite, with an alkali solution, and with water, successively. The carbon tetrachloride layer was concentrated to a mixture of the sulfoxide and the unchanged sulfide. Recrystallization of the mixture from n-hexane - benzene yielded (R)-(+)-benzyl p-tolyl sulfoxide, mp 142°C, $[\alpha]_D$ +143°(acetone), in 4% yield. Since the specific rotation of optically pure (R)-(+)-benzyl p-tolyl sulfoxide is reported to be $[\alpha]_D$ +252°(acetone),[7)] the optical yield of the sulfoxide obtained should be 56%. Table 1 summarizes typical data for the asymmetric oxidation of some sulfides in the presence of optically active alcohols whose absolute configurations have been known.

Table 1. Asymmetric oxidation of sulfides with NBC in the presence of optically active alcohols

				Sulfoxides			
Sulfides[a]	Alcohols (Abs.Config.)	Solvent	Time (hr)	Yield (%)	$[\alpha]_D$[e]	Opt.Yield[d] (%)	Abs.Config. Found(Expect.)
$p\text{-}CH_3C_6H_4SCH_2C_6H_5$	(-)-Menthol(R)[b]	CH_2Cl_2	70	47	+1.9°	0.8	R(R)
	(+)-2-Octanol(S)[c]	CH_2Cl_2	72	67	-0.3°	0.1	S(S)
	(-)-Menthol(R)	$CHCl_3$	70	2	+130.3°	52	R(R)
	(-)-Menthol(R)	CCl_4	70	4	+142.6°	56	R(R)
	(-)-Menthol(R)	Toluene	70	5	+102.0°	41	R(R)
$p\text{-}CH_3C_6H_4SCH_3$	(-)-Menthol(R)	CH_2Cl_2	70	45	+1.3°	1	R(R)
$C_6H_5SCH_3$	(-)-Menthol(R)	CH_2Cl_2	72	54	+1.9°	1.3	R(R)

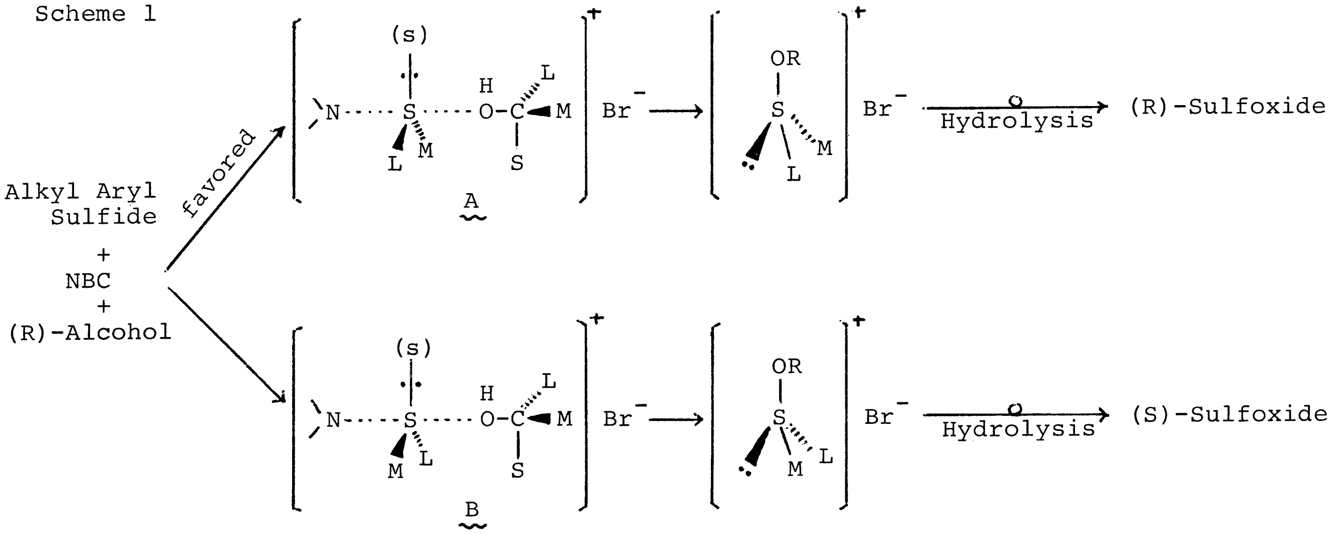
a) The reaction was carried out at -20°C. b) $[\alpha]_D$ -49.5°(EtOH). c) $[\alpha]_D$ +9.9°(neat). c) Calculated from the published data; (R)-(+)-benzyl p-tolyl sulfoxide $[\alpha]_D$ +252° (acetone)[C.J.M. Stirling, J. Chem. Soc., 1963, 5741], (R)-(+)-methyl p-tolyl sulfoxide $[\alpha]_D$ +146°(acetone),[8e] (R)-(+)-methyl phenyl sulfoxide $[\alpha]_D$ +149° (acetone)[J. Jacobs and K. Mislow, J. Amer. Chem. Soc., 89, 5228(1967)]. e) Determined in acetone.

As shown in Table 1, when the yields of sulfoxides are controlled less than 10%, the optical yields of the sulfoxides obtained are strikingly high. And the absolute configuration of the sulfoxides obtained depends on the chirality of the alcohols. Previously, the asymmetric oxidations of sulfides to sulfoxides with optically active peroxy-acids have been reported.[8] However, the optical yields reported are several per cent at most.

To interpret the stereochemical course of this asymmetric oxidation on the basis of these data, a model prediction like that proposed by Cram and Prelog[9] is attempted.[10] Recently, it has been reported that N-chlorosuccinimide readily reacts with a dialkyl sulfide to form an ionic adduct, dialkylimidosulfonium salt.[11] Supposing NBC and sulfides also form an adduct in the similar fashion to the case of N-chlorosuccinimide, two diastereomeric pathways may be drawn for this NBC-oxidation. (Scheme 1).[13] Since the relative steric bulk of the substituents on sulfur is considered to be lone pair < methyl < benzyl < aryl, the transition state represented as A would be kinetically favored by steric requirements. And the alkoxysulfonium salt12) produced via A will afford a sulfoxide which has the same chirality as that of the alcohol used, by hydrolysis.14)

Further investigation on this oxidation is now underway in our laboratory.

Scheme 1



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9) J.D. Morrison and H.S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Inc., Englewood Cliffs, New Jersey (1971).

10) For the asymmetric oxidation of sulfides with optically active peroxy-acids, an analogous model prediction was conducted by Montanari et al..[8a-c)]

11) E. Vilsmaier and W. Sprügel, Tetrahedron Lett., 1972, 625.

12) It has been known that the alkoxysulfonium salt is an intermediate of halogen oxidation of sulfides to sulfoxides in the presence of alcohol; e.g., C.R. Johnson and J.J. Rigau, J. Amer. Chem. Soc., 91, 5398(1969); C.R. Johnson, C.C. Bacon, and W.D. Kingsbury, Tetrahedron Lett., 1972, 501

13) Recently, E.D. Corey et al. have reported that the reaction of alcohols with the complex, $(CH_3)_2\overset{+}{S}\text{-X}\ Cl^-$ (X; succinimido), formed from N-chlorosuccinimide and dimethyl sulfide affords the corresponding sulfonium salts, $(CH_3)_2\overset{+}{S}\text{-OCHR}_1R_2\ Cl^-$, and found that the sulfonium salts decompose to the corresponding halides and dimethyl sulfoxide, when the salts are unstable. [E.J. Corey, C.U. Kim and M. Takeda, Tetrahedron Lett., 1972, 4339]. However, it seems that the decomposition of this kind does not take place in the present reaction.

14) The hydrolysis of alkoxysulfonium salts is considered to proceed with inversion of configuration at the sulfur atom. [C.R. Johnson and D. McCants,Jr., J. Amer. Chem. Soc., 87, 5404(1965); C.R. Johnson, ibid., 85, 1020(1963); N.J. Leonard and C.R. Johnson, ibid., 84, 3701(1962)].

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