CHEMISTRY LETTERS, pp. 563-566, 1976. Published by the Chemical Society of Japan

ASYMMETRIC OXIDATION OF SULFIDES WITH AN OPTICALLY ACTIVE SUBSTITUTED N-HALOGENOCAPROLACTAM

Yoshiyasu SATO, Norio KUNIEDA, and Masayoshi KINOSHITA
Department of Applied Chemistry, Faculty of Engineering,
Osaka City University, Sumiyoshi-ku, Osaka 558

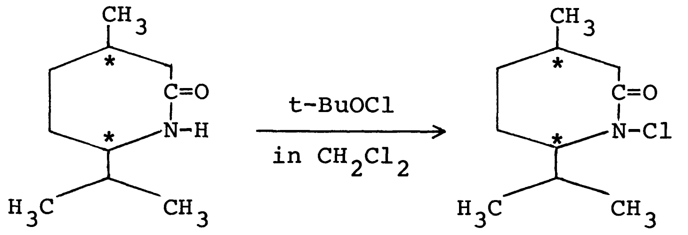
Oxidation of sulfides using an optically active substituted N-halogenocaprolactam, (+)-N-chloro-7-isopropyl-4-methyl-2-oxohexamethyleneimine, produces the corresponding optically active sulfoxides. The absolute configuration of sulfoxides obtained depends on the chirality of the caprolactam used. The steric course of this asymmetric oxidation is discussed.

The asymmetric oxidation of sulfides has most frequently been accomplished by using a number of chiral peracids.$^{1-4)}$ A correlation model was proposed based on principles of steric control like those developed by Cram and Prelog$^{5)}$ in asymmetric syntheses at carbons.

We have previously reported$^{6)}$ that the oxidation of sulfides with N-bromo-ε-caprolactam (NBC) in the presence of optically active alcohols gave the corresponding optically active sulfoxides. The absolute configuration of sulfoxides obtained depends on the chirality of alcohols used. Present communication reports on the asymmetric oxidation of sulfides with an optically active substituted N-halogenocaprolactam, (+)-N-chloro-7-isopropyl-4-methyl-2-oxohexamethyleneimine (I), prepared by the chlorination of the corresponding (-)-imine (II) with tert-butyl hypochlorite in methylene chloride. The N-chloro-imine (I) was used without purification because it easily decomposed on heating.

To a solution of a sulfide (20 mmol) and (I) (20 mmol) in 200 ml of a solvent was added 8 ml of methanol with stirring at the desired temperature. After being stirred for the desired time, the reaction mixture was poured into a large amount of aqueous sodium thiosulfate to decompose unreacted (I). The sulfoxide was isolated by means of chromatography on silica gel eluting with benzene-ether (2 : 3).

The results of the asymmetric oxidation are summarized in Table 1.



(II)

M.p. 119-120°C,

$[\alpha]_D$ -50.86° (acetone)

(I)

M.p. 19.5-20.0°C,

$[\alpha]_D$ +34.75° ($CHCl_3$)

Analyses, % found(calcd).

	C	H	N
I[a]	57.90 (58.88)	8.55 (8.33)	6.74 (6.87)
II	70.47 (70.96)	11.46 (11.32)	8.18 (8.28)

a) Crude product

Table 1. Asymmetric Oxidation of Sulfides with (I)

Sulfide	Solvent	Temp. (°C)	Reaction Time (hr)	Sulfoxide Yield (%)	[α]$_D$ (°)	Opt.Yield[c] (%)	Abs. Config.
p-$CH_3C_6H_4SCH_2C_6H_5$	CH_2Cl_2	-40	24	45.0	0[a]	0	——
	CH_2Cl_2	-78	48	32.2	+ 1.14[a]	0.45	R
	Toluene	-78	60	7.4	+ 6.96[a]	2.76	R
p-$CH_3C_6H_4SC_6H_5$	Benzene	25	12	27.9	+ 0.34[a]	1.60	R
$C_6H_5SCH_3$	Toluene	-78	70	4.4	+ 0.39[a]	0.26	R
$C_6H_5CH_2SCH_3$	Toluene	-78	70	25.9	- 0.43[b]	0.45	R

a) Determined in acetone. b) Determined in ethanol.

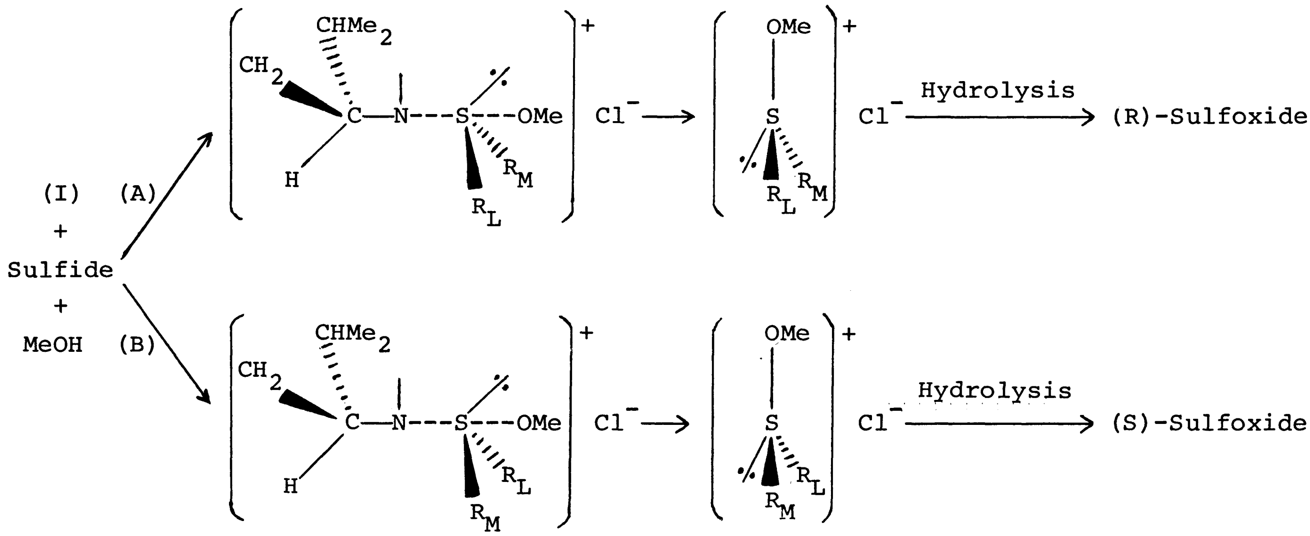
c) Calculated from the published data; (R)-(+)-benzyl p-tolyl sulfoxide $[\alpha]_D$ +252° (acetone),7) (R)-(+)-phenyl p-tolyl sulfoxide $[\alpha]_D$ +21.2° (acetone),8) (R)-(+)-methyl phenyl sulfoxide $[\alpha]_D$ +149° (acetone),9) and (S)-(+)-benzyl methyl sulfoxide $[\alpha]_D$ +96° (ethanol).4)

As shown in Table 1, in the case of aryl or alkyl benzyl sulfides the oxidation must be carried out below -40°C in order to afford optically active sulfoxides.

The substituted caprolactam (II), prepared from ℓ-menthol by means of the method of M. Imoto et al.,10) has two asymmetric centers at 4- and 7-positions of the ring. The asymmetric carbon at 7-position has (S)-configuration.11) The sulfoxides obtained have the (R)-configuration on the sulfur atom in all cases.

On the basis of these results, a transition state model like that proposed by Prelog[5)] is proposed to interpret the steric course of this asymmetric oxidation. Recently, it has been reported that N-chlorosuccinimide or 1-chlorobenzotriazole reacts with sulfides to form an imido- or an iminosulfonium salt.[12,13)] Assuming the similar ionic adduct in the present reaction, two diastereomeric pathways may be drawn in a similar manner as described previously (Scheme 1).

Scheme 1.



According to this model, pathway (A) is preferred since the approach of the asymmetric reagent to a sulfide is such that the large group ($-CHMe_2$) attached to the chiral center is more easily arranged between the smaller group (lone pair) and the middle group (R_M) of the sulfide, rather than between the smaller and the larger (R_L). And the resulting alkoxysulfonium salts afford sulfoxides by hydrolysis, proceeding with inversion of configuration.[14-16)] Thus the sulfoxide with (R)-configuration is produced in excess.

Further investigation on the other asymmetric reaction with this optically active substituted caprolactam is now underway.

REFERENCES

1) A. Maccioni, F. Montanari, M. Secci, and M. Tramontini, Tetrahedron Lett., 1961, 607.

2) U. Folli, D. Iarossi, F. Montanari, and G. Torre, J. Chem. Soc.(C), 1968, 1317.

3) A. Mayr, F. Montanari, and M. Tramontini, Gazz. Chim. Ital., 90, 739(1960).

4) K. Mislow, M. Green, and M. Raban, J. Amer. Chem. Soc., 87, 2761(1965).

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

6) M. Kinoshita, Y. Sato, and N. Kunieda, Chem. Lett., 1974, 377.

7) C. J. M. Stirling, J. Chem. Soc., 1963, 5741.

8) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay,Jr., J. Amer. Chem. Soc., 87, 1958(1965).

9) J. Jacobs and K. Mislow, J. Amer. Chem. Soc., 89, 5228(1967).

10) M. Imoto, H. Sakurai, and T. Kono, J. Polym. Sci., 50, 467(1961).

11) G. G. Lyle and R. M. Barrera, J. Org. Chem., 29, 3311(1964).

12) E. J. Corey, C. U. Kim, and M. Takeda, Tetrahedron Lett., 1972, 4339.

13) C. R. Johnson, C. C. Bacon, and W. D. Kingsbury, ibid., 1972, 501.

14) C. R. Johnson and D. McCants,Jr., J. Amer. Chem. Soc., 87, 5404(1965).

15) C. R. Johnson, ibid., 85, 1020(1963).

16) N. J. Leonard and C. R. Johnson, ibid., 84, 3701(1962).

(Received April 12, 1976)