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The Reaction of Elemental Sulfur with Organic Compounds. V. Reactions of Optically Active Sulfoximine with Elemental Sulfur and with Diphenyl Disulfide[1]

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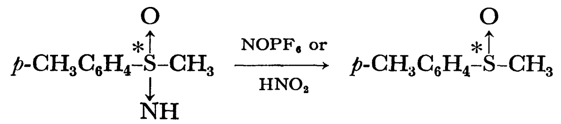
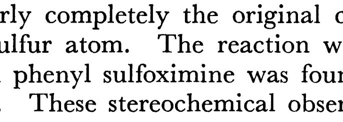
The stereochemistry of sulfur compounds having S–N bonds such as sulfilimine and sulfoximine has recently drawn considerable attention.[2–7] Cram and his coworkers reported a stereospecific cleavage of S–N bond of sulfoximine with $NOPF_6$ or HNO_2 to afford the corresponding sulfoxide having the same configuration as that of the original sulfoximine.[2,3]



$$p\text{-}CH_3C_6H_4\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{NH}{\downarrow}}{\overset{*}{S}}}\text{-}CH_3 \xrightarrow[HNO_2]{NOPF_6\text{ or}} p\text{-}CH_3C_6H_4\text{-}\overset{\overset{O}{\uparrow}}{\overset{*}{S}}\text{-}CH_3$$

We reported a convenient method of deimination of sulfoximine by treatment with elemental sulfur or diphenyl disulfide to the corresponding sulfoxide in nearly quantitative yield.[1] In this paper we report on a stereochemical course and plausible mechanism of the reaction.



$$R\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{NH}{\downarrow}}{S}}\text{-}R' \xrightarrow[PhSSPh]{S_8\text{ or}} R\text{-}\overset{\overset{O}{\uparrow}}{S}\text{-}R'$$

1: $R{=}p\text{-}CH_3C_6H_4\text{-}$, $R'{=}CH_3\text{-}$
2: $R{=}Ph\text{-}$, $R'{=}CH_3\text{-}$

The results of the reaction with optically active methyl *p*-tolyl sulfoximine are shown in the table. We see that the reaction proceeds stereospecifically retaining nearly completely the original configuration around the sulfur atom. The reaction with optically active methyl phenyl sulfoximine was found to give a similar result. These stereochemical observations suggest that the hybridization at sulfur atom of sulfoximine is left undisturbed in the course of the reaction.[8] A conceivable mechanistic pathway is shown below.

In view of the basic nature of the imino group of sulfoximine,[9] the initial step of the reaction is considered to involve a nucleophilic attack of the nitrogen atom of sulfoximine on the sulfur atom of S–S bond forming a dipolar intermediate (**3**). In the following step, **3** would decompose through the attack of thiolate anion on the nitrogen atom eventually cleaving off

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[1] Paper IV; S. Oae, Y. Tsuchida, K. Tsujihara, and N. Furukawa, This Bulletin, **45**, 2856 (1972).

[2] D. J. Cram, J. Day, D. R. Rayer, D. M. von Schriltz, D. J. Duchamp, and D. C. Garwood, *J. Amer. Chem. Soc.*, **92**, 7369 (1970).

[3] T. R. Williams, R. E. Booms, and D. J. Cram, *ibid.*, **93**, 7338 (1971).

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[5] C. W. Schroeck and C. R. Johnson, *ibid.*, **93**, 5305 (1971).

[6] E. U. Jonsson, C. C. Bacon, and C. R. Johnson, *ibid.*, **93**, 5306 (1971).

[7] E. U. Jonsson and C. R. Johnson, *ibid.*, **93**, 5308 (1971).

[8] For detailed accounts of substitution on sulfur atom; a) S. Oae, *Quart. Reports on Sulfur Chem.*, **5**, 53 (1970); b) see Ref. 2).

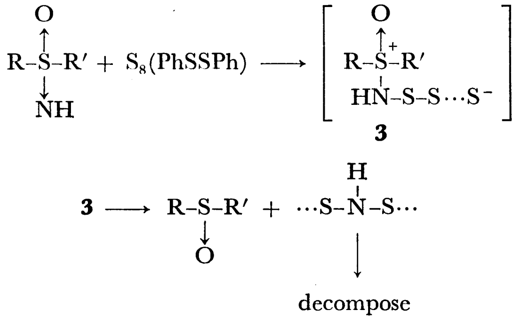
[9] S. Oae, K. Tsujihara, and N. Furukawa, *Chem. Ind.* (London) **1968**, 1596.

Table 1. Reaction of optically active sulfoximine

Reaction	$[\alpha]_D$ (optical purity)	Condition	Product	$[\alpha]_D$ (Optical purity)
(−)-(*R*)-**1**+S_8	−33.4° (100%)	neat 160°C 10 min	(+)-(*R*)-*p*-TolS(O)CH_3	+147° (98%)
(−)-(*R*)-**1**+PhSSPh	−33.4° (100%)	*o*-$C_6H_4Cl_2$ reflux 18 hr	(+)-(*R*)-*p*-TolS(O)CH_3	+148° (99%)
(+)-(*S*)-**2**+S_8	+33.8°	neat 160°C 10 min	(−)-(*S*)-PhS(O)CH_3	−141° (95%)

p-Tol=*p*-$CH_3C_6H_4$-

sulfoxide.[10] Thus the sulfoxide formed can maintain the same configuration as that of sulfoximine.



Experimental

Materials. Optically pure (−)-(*R*)-methyl *p*-tolyl sulfoximine ((−)-(*R*)-**1**) was prepared from optically pure (+)-(*R*)-methyl *p*-tolyl sulfoxide ($[\alpha]_D$=+150°, *c* 0.67, acetone) according to the method used by Cram *et al.*[2] $[\alpha]_D$=−33.4° (*c* 1.86, acetone); lit, $[\alpha]_D$=−33.4° (*c* 2.275, acetone).

(+)-(*S*)-Methyl phenyl sulfoximine ((+)-(*S*)-**2**) was prepared through resolution of sulfoximine according to the method used by Fusco and Tenconi.[11] To a solution of *d*-camphor-10-sulfonic acid (15 g) in ethanol was added methyl phenyl sulfoximine (6.5 g) and the mixture was refluxed for an hour. Acetone (50 ml) was then added to the reaction mixture and cooled in a refrigerator overnight. The crystals deposited were collected by filtration and recrystallized several times from a mixture of acetone–ethanol: mp 176°C, $[\alpha]_D$=+45.3° (methanol). The salt of sulfoximine-*d*-camphor-10-sulfonic acid was dissolved in a cold dilute sodium hydroxide solution and extracted with chloroform, washed with water and dried over anhydrous magnesium sulfate. After the solvent was evaporated, oily (+)-(*S*)-**2** was obtained and used for the reaction without further purification. $[\alpha]_D$=−33.8° (*c* 3.62, acetone).

Elemental sulfur was purified by recrystallization of commercial sulfur from benzene: mp 114°C.

Diphenyl disulfide was prepared from thiophenol by iodine oxidation in water: mp 61°C.

*Reaction of (−)-(*R*)-**1** with Sulfur.* A mixture of 0.153 g (1 mmol) of (−)-(*R*)-**1** and 0.032 g (1 mg-atom) of sulfur was placed in a glass tube and heated in an oil bath maintained at *ca.* 160°C for 10 min. The red colored product was chromatographed on silica gel with chloroform as an eluent. Methyl *p*-tolyl sulfoxide was obtained as the main product in an almost quantitative yield. After recrystallization several times from ether–hexane, the optical rotation was measured; $[\alpha]_D$=+147° (*c* 0.54, acetone). The sulfoxide was 98% optically pure. Since the starting sulfoximine was nearly optically pure, the reaction is 98% stereospecific.

*Reaction of (−)-(*R*)-**1** with Diphenyl Disulfide.* Diphenyl disulfide, 0.218 g (1 mmol), and (−)-(*R*)-**1**, 0.153 g (1 mmol) were dissolved in 5 ml of *o*-dichlorobenzene and refluxed for about 18 hr. The product was treated in a similar manner to that described above and the sulfoxide was obtained in 99% optical purity. $[\alpha]_D$=+148° (*c* 0.63, acetone).

*Reaction of (+)-(*S*)-**2** with Sulfur.* This reaction was carried out in a similar manner to that described. After chromatography oily sulfoxide was obtained and the optical rotation was measured without further purification. $[\alpha]_D$=141° (*c* 19.3, ethanol) 95% optically pure (optically pure methyl phenyl sulfoxide, $[\alpha]_D$=149°[12]).

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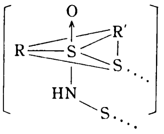
[10] There is the possibility of substitution on the sulfur atom. If the nucleophilic attack of thiolate anion on the sulfur atom of **3** should occur to form a hypothetical pentacoordinated sulfur intermediate (**4**), the configuration of the resulting sulfoxide would be either retained, inverted or racemized depending on the mode of displacement on the sulfur atom. However, such a valence expanded sulfur intermediate is not necessary for interpreting the results of the stereochemistry of the reaction of optically active sulfoximine with sulfur or diphenyl disulfide.



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