Nucleophilic Substitution of Tricoordinate Sulfur Atom of Sulfonium Salt with Retention of Configuration.[1] Different Stereochemistry of Substitution by Amidate Anions

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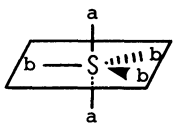
Optically active *N*-substituted *S*-(*o*-methoxyphenyl)-*S*-phenylsulfilimines were obtained in moderate yields upon simple treatment of a mixture of *o*-methoxyphenyl phenyl sulfide and *t*-butyl hypochlorite in the presence of *l*-menthol and followed by amidate anions. Although some sulfilimines (*N*-tosyl-, *N*-benzoyl-, and *N*-(chloroacetyl)sulfilimines) were found to be rich in *S*-configuration around the sulfur atom, the others (*N*-(dichloroacetyl)-, *N*-(trichloroacetyl)-, and *N*-(trifluoroacetyl)sulfilimines) were found to be rich in *R*-configuration around the sulfur atom. In the displacement of *l*-menthyloxy group on the sulfur atom of the incipiently formed *l*-menthyloxysulfonium salt with *p*-toluenesulfonamidate, benzamidate, and chloroacetamidate anions, the respective *N*-acylsulfilimines of *S*-configuration were obtained by substitution with inversion of configuration, while *N*-acylsulfilimines having *R*-configuration were obtained by substitution of the same *l*-menthyloxysulfonium salt by polyhaloacetamidate anions such as dichloroacetamidate, trichloroacetamidate, and trifluoroacetamidate anions, with retention of configuration.

The mechanism of nucleophilic substitution reaction at the tricoordinate sulfur atom has been a subject of considerable interest.[2] One of the important problems is the structure of the transition state or the intermediate and the stereochemical course of the nucleophilic substitution on the sulfur atom. The nucleophilic substitution of the tricoordinate sulfur atom has been suggested to proceed *via* formation of a sulfurane type intermediate of trigonal bipyramidal structure shown below, and the stereochemistry of the substitution which involves the initial formation of a σ-sulfurane is believed to be determined by the relative orientation of the attacking nucleophile and the leaving group. In the hypervalent σ-sulfurane, the apical bond is presumed to be made up with a *p*-orbital, and hence is longer and more polar than the basal bond which is composed mainly of sp^2 hybrid.



NUCLEOPHILE	LEAVING GROUP	STEREOCHEMISTRY
a	a	INVERSION
b	b	INVERSION
a	b	RETENTION
b	a	RETENTION

Fig. 1. The relation between the stereochemistry and the orientation of the nucleophile and the leaving group.

Therefore both the entering nucleophile and the leaving group are considered to be placed at apical positions in the nucleophilic substitution on the tricoordinate sulfur atom. When there is no special interaction between the entering nucleophile and the leaving group, both groups will be placed at the apical positions of opposite directions, inversion of configuration on the sulfur atom will be the rational course.

Inversion of configuration would also be resulted, if both entering and leaving groups would occupy the basal positions.

However, this orientation is quite unlikely, since both entering and leaving groups are relatively more polar and their bonds are longer than others and hence should be placed at the apical rather than at the basal positions at the transition state of the nucleophilic substitution on the tricoordinate sulfur atom. Meanwhile, if there is any special interaction between the entering nucleophile and the leaving group, in the resulted sulfurane type intermediate, the nucleophile which enters from the apical position and the leaving group at the basal position may turn their positions by pseudorotation before placing the entering nucleophile at a basal position and extruding the leaving group from an apical position, retention of configuration is expected to be observed (Fig. 1).

Since the first example of inversion at the sulfur atom was found in the transesterification of a chiral sulfite,[3] numerous instances of nucleophilic substitution reaction have been demonstrated to occur with inversion of configuration on the sulfur,[4] and this is

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believed to be the most common stereochemical course for the nucleophilic substitution (ligand exchange) on the sulfur atom. However, there have been a few cases in which retention of configuration has been observed in the nucleophilic substitution on the tricoordinate sulfur atom. Oae *et al.* were the first who observed that optically active methyl *p*-tolyl sulfoxide labeled with ^{18}O undergoes the oxygen exchange with that of dimethyl sulfoxide without any loss of optical activity, *i.e.*, the retention of configuration on the sulfur atom.[5] In this case a dipole-dipole interaction between the two sulfoxide linkages is considered to keep the two ligands at nearly 90° angle throughout the ligand exchange. Since then the retention of configuration in nucleophilic substitution has also been observed in the several reactions, such as in the conversion of chiral sulfoxides into the corresponding sulfilimines in the reactions with *N*-sulfinyl-*p*-toluenesulfonamide,[6] *N,N'*-ditosylsulfur diimide,[7] and *p*-toluenesulfinylnitrene[8] as reagents. Moreover, the reaction of an optically active amidothiosulfite with mercury(II) chloride leading to the optically active aminosulfinyl chloride was shown to proceed with retention of configuration at the sulfur center.[9]

Recently, a few other reactions also have been reported to proceed with retention of configuration on the sulfur atom.[10]

In all these reactions involving the trigonal bipyramidal intermediates, formation of four-membered ring by a special interaction between leaving and entering groups at the apical and basal positions is generally believed to be the main factor responsible for the retention mechanism.

Recently, we have reported that optically active (*S*)-(−)-*S*-(*o*-methoxyphenyl) (or *o*-methylphenyl)-*S*-phenyl-*N*-tosylsulfilimine was obtained by simple treatment of an equimolar mixture of *l*-menthol and the corresponding sulfide at first with *t*-butyl hypochlorite and subsequent addition of sodium *N*-*p*-toluenesulfonamidate at a low temperature, as shown in Fig. 2. When we used some other nucleophiles instead of the amidate anion, we were able to obtain other optically active diaryl tricoordinate sulfur compounds; namely, when hydroxide anion was used, the corresponding (*S*)-(−)-sulfoxide of inverted configuration was obtained whereas in the teatment of malonate anion, the corresponding inverted (+)-sulfonium ylide was also obtained.[11] In all these reactions, optically active *l*-menthyloxysulfonium chloride is presumed to be formed as the incipient intermediate (Fig. 2). This method has now become a simple and hence the most general preparative method to synthesize optically active (*o*-substituted aryl) phenyl tricoordinate sulfur compounds. However, when such polyhaloacetamidates such as dichloro-, trichloro-, and trifluoroacetamidate anions were used instead of *p*-toluenesulfonamidate anion, we have obtained unexpectedly the corresponding sulfilimines each having excess of the R-configuration in good yields.[1] In this papar we wish to report this new type of nucleophilic substitution at the tricoordinate sulfur atom and the mechanism of this unusual stereochemistry.

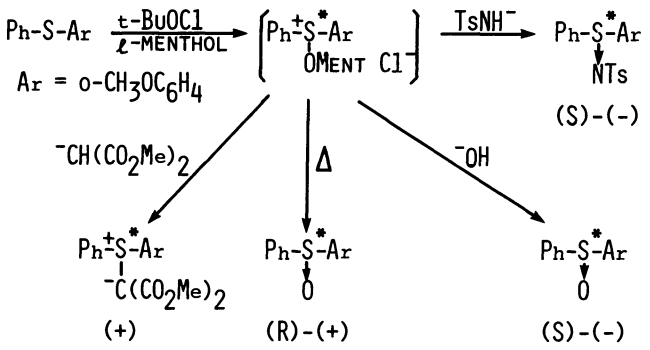
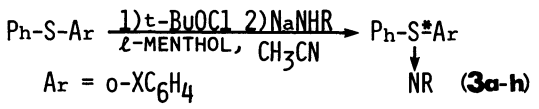


Fig. 2. Asymmetric syntheses of some optically active tricoordinate sulfur compounds.

Results and Discussion

Unsymmetrical *S,S*-diarylsulfilimines were obtained in moderate yields by treating an equimolar mixture of *l*-menthol and the corresponding sulfide first with *t*-butyl hypochlorite and subsequently with amidate anions as shown in Scheme 1.

The *N*-tosylsulfilimines (**3a** and **g**), *N*-benzoylsulfilimine (**3b**), and *N*-(chloroacetyl)sulfilimine (**3c**) thus obtained showed minus sign of optical rotation, and *N*-(polyhaloacetyl)sulfilimines such as *N*-(dichloroacetyl)-(**3d**), *N*-(trichloroacetyl)-(**3e**), and *N*-



Scheme 1.

Table 1. Asymmetric syntheses of *N*-substituted *S*-(*o*-methoxyphenyl)-*S*-phenylsulfilimines (**3a—h**)

	X-	R	Yield/%	$[\alpha]_D$/°	e.e./%
3a	CH_3O-	Ts	47	−39.0	40.4[a]
3b	CH_3O-	COPh	65	−17.3	27.3
3c	CH_3O-	$COCH_2Cl$	47	−45.5	35.5
3d	CH_3O-	$COCHCl_2$	34	+11.7	12.5
3e	CH_3O-	$COCCl_3$	72	+26.4	47.2
3f	CH_3O-	$COCF_3$	53	+35.4	47.2
3g	CH_3-	Ts	72	−14.4	35.1[a]
3h	CH_3-	$COCF_3$	96	+20.9	26.4

a) This value was calculated optical purity.

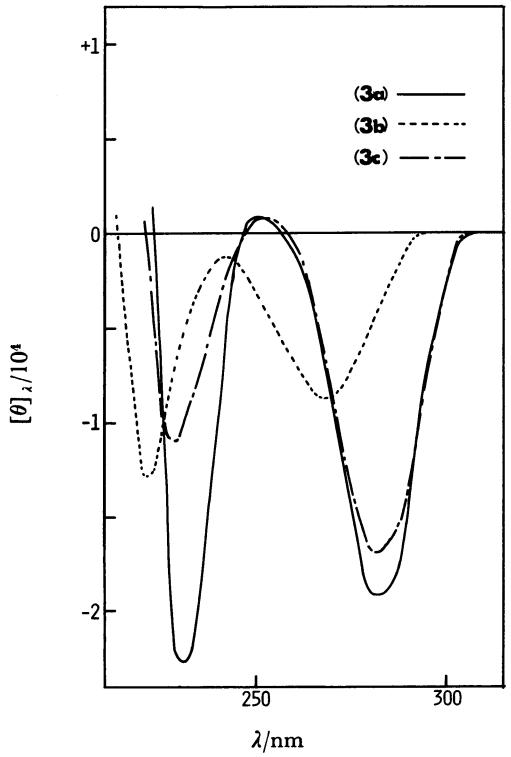


Fig. 3a. CD spectra of (*S*)-(−)-*S*-(*o*-methoxyphenyl)-*S*-phenyl-*N*-tosyl-(**3a**), (*S*)-(−)-*N*-benzoyl-(**3b**), and (*S*)-(−)-*N*-(chloroacetyl)-(**3c**) sulfilimines.

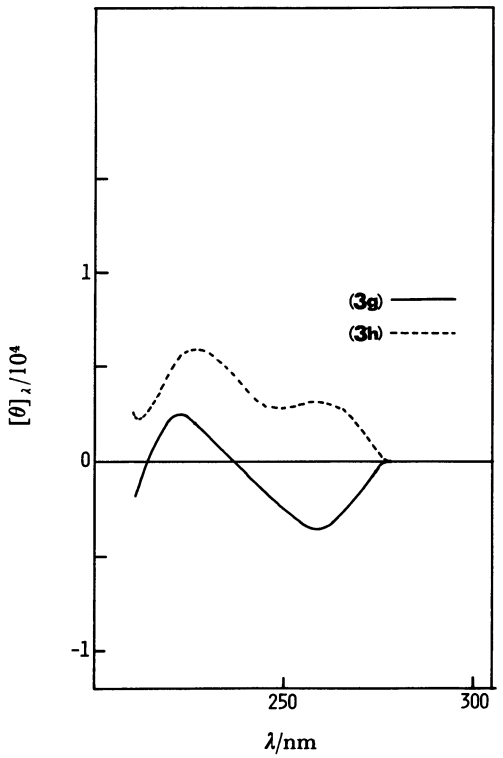


Fig. 3c. CD spectra of (*S*)-(−)-*S*-(*o*-methylphenyl)-*S*-phenyl-*N*-tosylsulfilimine (**3g**) and (*R*)-(+)-*N*-(trifluoroacetyl)sulfilimine (**3h**).

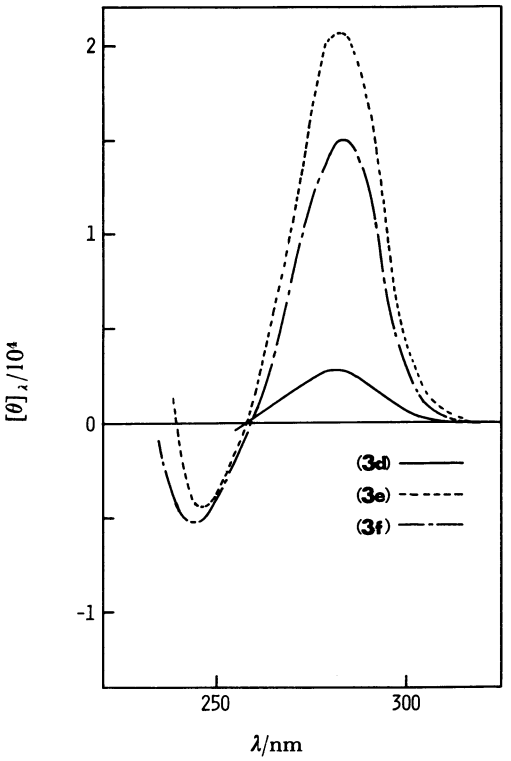


Fig. 3b. CD spectra of (*R*)-(+)-*S*-(*o*-methoxyphenyl)-*S*-phenyl-*N*-(dichloroacetyl)-(**3d**), *N*-(trichloroacetyl)-, (**3e**), and *N*-(trifluoroacetyl)-(**3f**) sulfilimines.

(trifluoroacetyl)sulfilimines (**3f** and **h**) showed plus sign of optical rotation. The configurations of these sulfilimines were determined by comparing their circular dichroism (CD) spectra with that of (−)-**3a** which was determined to be of *S*-configuration by X-ray crystallographic analysis.[12] The CD spectra of these sulfilimines, thus obtained, are shown in Fig. 3. Meanwhile, the configurations of sulfilimines (**3b—f**) were also determined by comparing the optical rotations with those of the authentic samples. The authentic samples were prepared by acylating of optically active (*S*)-(−)-S-(*o*-methoxyphenyl)-*S*-phenylsulfilimine formed upon treatment of (*S*)-(−)-*S*-(*o*-methoxyphenyl)-*S*-phenyl-*N*-tosylsulfilimine with concd sulfuric acid, as shown in Scheme 2. The sulfilimines thus obtained are listed in Table 2. The assignment of the configuration of each of these sulfilimines (**3b—f**) determined by the CD spectrum was in good agreement with the result obtained by comparison with the optical rotation of the authentic sample.

Based on these observations the sulfilimines having minus optical rotations (**3a—c** and **g**) obtained in this reaction, are considered to have the *S*-configuration, while those having plus optical rotations (**3d—f** and **h**) are determined to have the *R*-configuration. Thus, the sulfilimines prepared by treatment of the *l*-menthyloxysulfonium salt (**2**) with such amidate

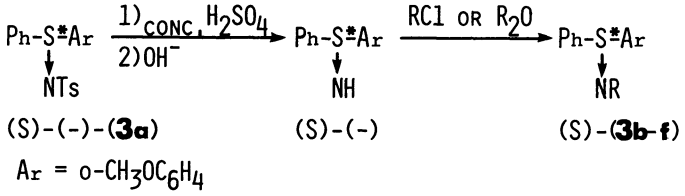
Table 2. Syntheses of authentic samples

4 $[\alpha]_D$/°	Acylating reagent		Sulfilimines R	Yield/%	$[\alpha]_D$/°	Mp θ_m/°C
−194	$(PhCO)_2O$	**3b**	PhCO	55	−76	99—99.5
−187	$ClCH_2COCl$	**3c**	$ClCH_2CO$	86	−89	Oil
−33	$Cl_2CHCOCl$	**3d**	Cl_2CHCO	62	−16	116—118
−33	$(Cl_3CCO)_2O$	**3e**	Cl_3CCO	35	−13	122—124
−187	$(F_3CCO)O$	**3f**	F_3CCO	75	−76	Oil

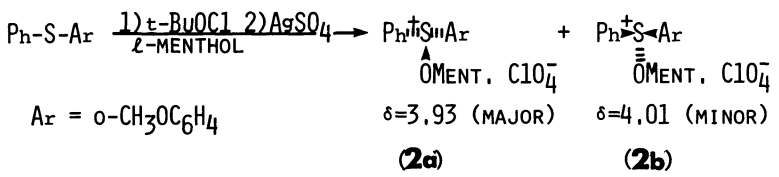
anions as *p*-toluenesulfonamidate, benzamidate, and chloroacetamidate have in excess of those of the *S*-configuration, while the sulfilimines prepared by the reaction of **2** with amidate anions having highly electron-withdrawing acyl groups such as dichloroacetamidate, trichloroacetamidate, and trifluoroacetamidate have in excess of those of the *R*-configuration. In order to scrutinize the stereochemistry of these substitutions, we have made an attempt to isolate the key intermediate, namely *o*-methoxyphenylphenyl-*l*-menthyloxysulfonium salt and investigated the stereochemical course of the nucleophilic substitution of the sulfonium salt with various amidate anions. *o*-Methoxyphenylphenyl-*l*-menthyloxysulfonium salt was obtained as perchlorate (**2**) by treating an equimolar mixture of *o*-methoxyphenyl phenyl sulfide and *l*-menthol, at first with *t*-butyl hypochlorite and subsequent addition of silver perchlorate as shown in Scheme 3. The sulfonium salt (**2**) thus obtained was found to be a mixture of two

Table 3. Diastereomer ratio of *l*-menthyloxysulfonium perchlorate

Solvent	Temperature/°C	Yield/%	*R*/*S*
CH_3CN	−40	84	75/25
THF	−60	36	75/25
$(CH_3)_2O$	−60	67	58/42
CH_2Cl_2	−60	89	78/22
CH_2Cl_2	−80	67	84/16



Scheme 2.



Scheme 3.

Table 4. Reaction of amidate anions with *l*-menthyloxysulfonium perchlorate (**2**)[a)]

R/*S* of 2	Solvent	R	Yield/%	$[\alpha]_D^{20}$/°	e.e./%	o.p./%
83/17	CH_3CN-DMF	Ts	5	−43	44	60
70/30	CH_3CN	$COCH_2Cl$	58	−9	7	18
78/22	CH_3CN	$COCHCl_2$	51	+5	5	9
83/17	CH_3CN	$COCCl_3$	39	+16	44	66
83/17	CH_3CN	$COCF_3$	60	+33	40	58

a) Reaction temperature was −35 °C.

diastereomers, since the sulfonium salt (**2**) has two chiral centers, namely the sulfonium sulfur atom and the carbon atom of *l*-menthyloxy group attached to the oxygen atom. The ratio of the two diastereomers thus obtained was determined by the ^{1}H NMR integration of the peaks of *o*-methoxyl groups appeared at δ 3.93 for the major diastereomer and δ 4.01 for the minor one. However, the diastereomeric ratio of 2 was found to change with the change of solvent and reaction temperature in the treatment with *t*-butyl hypochlorite as shown in Table 3. When an amidate anion was added into the acetonitrile solution of the sulfonium salt (**2**), the corresponding sulfilimine was obtained as summarized in Table 4. Their optical yields are rather low, however, the stereochemical course for the substitution is in good agreement with the result obtained from the direct asymmetric induction shown in Table 1; namely, the corresponding *N*-tosyl-(**3a**) and *N*-(chloroacetyl)sulfilimine (**3c**) have the *S*-configuration, and *N*-(dichloroacetyl)-(**3d**), *N*-(trichloroacetyl)-(**3e**), and *N*-(trifluoroacetyl)sulfilimines (**3f**) show the *R*-configuration. These observations clearly indicate that the *l*-menthyloxysulfonium salt (**2**) is the key intermediate in the asymmetric reaction as shown in Scheme 1.

Table 5. Optical yields of asymmetric syntheses of sulfilimines (**3a—f**)

	R	e.e./%	o.p./%
3a	Ts	40.4	81
3b	COPh	27.3	55
3c	$COCH_2Cl$	35.5	71
3d	$COCHCl_2$	12.5	25
3e	$COCCl_3$	47.2	94
3f	$COCF_3$	47.2	94

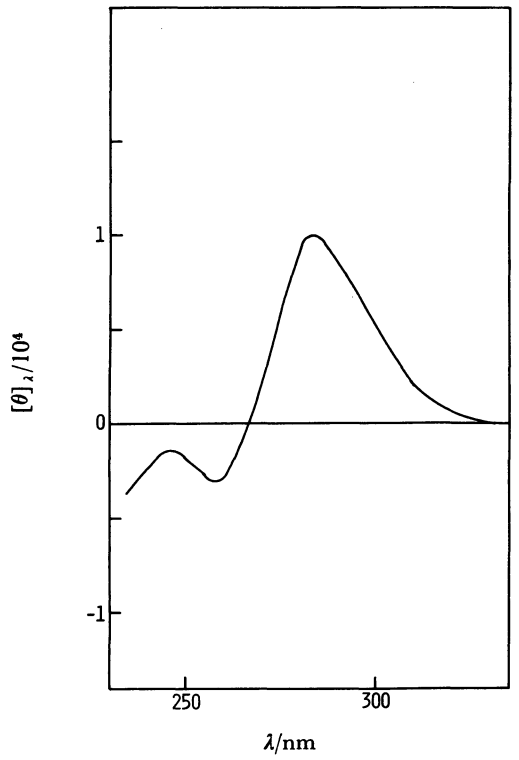


Fig. 4. CD spectra of (*l*-menthyloxy)(*o*-methoxyphenyl)phenylsulfonium perchlorate (2).

When *t*-butyl hypochlorite was added at −40°C into the acetonitrile solution of the equimolar mixture of sulfide (**1**) and *l*-menthol, namely under the same conditions as the results shown in Table 1 and the ratio of the two diastereomers was found to be 75 : 25. Thus, the optical yields in the asymmetric syntheses of these sulfilimines shown in Table 1 have been determined and the results are summarized in Table 5. The CD spectrum of *l*-menthyloxysulfonium perchlorate (**2**) is shown in Fig. 4. From the CD curve, the configuration around the sulfur atom of the *l*-menthyloxysulfonium perchlorate (**2**) was determined to be excess of the *R*-configuration, in accordance with the result reported previously by us.[11a] Therefore, the sulfilimines having the opposite sign of the Cotton effect to that of the sulfonium perchlorate (**2**), namely, *N*-tosyl-(**3a**), *N*-benzoyl-(**3b**), and *N*-(chloroacetyl)sulfilimines (**3c**) are undoubtedly obtained through the inversion process. When the sulfilimines showing the same sign of the Cotton effect to that of the sulfonium perchlorate (**2**), namely *N*-(dichloroacetyl)-, (**3d**), *N*-(trichloroacetyl)-(**3e**), and *N*-(trifluoroacetyl)-sulfilimines (**3f**) are obviously formed through the retention process stereochemically. Thus, it appears that the retention process predominates over the inversion process when the more acidic amidate anion is used. Accordingly, some reported pK_a values for the conjugated acids of amides which were used in this experiment have been sought out, as shown in the following, namely $PhCONH_3^+$=−1.55,[13] $ClCH_2CONH_3^+$−3.21,[14] *p*-$TolSO_2$ NH_3^+=−3.3,[15] $Cl_2CHCONH_3^+$<−6.4.[14]

These data sugggest that the stereochemistry of substitution of the *l*-menthyloxysulfonium salt with the amidate anion seems to be related to the acidity of the amide. Namely, the ordinary amidate anion seems to substitute *l*-menthyloxy group of *l*-menthyloxysulfonium salt with inversion of the configuration, while the more acidic amidate anion seems to undergo substitution with retention of the configuration.

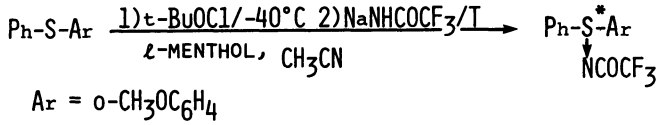
The effect of temperature on the stereochemistry of the reaction was also examined. In order to fix the *R*/*S* ratio of the intermediate, *i.e.*, the *l*-menthyloxysulfonium ion, *t*-butyl hypochlorite was added under a certain fixed conditions. Then, after changing the temperature of the whole mixture,

sodium trifluoroacetamidate was added into the system as shown in Scheme 4. The enantiomeric excess of the *N*-(trifluoroacetyl)sulfilimine thus obtained has been found to decrease with the increase of the reaction temperature as shown in Table 6. The decrease of *R/S* ratio with the increase of temperature could be resulted by the thermal racemization of the intermediate sulfonium salt. However, since the *R/S* ratio was found not to change from −30 °C to 42 °C, the thermal racemization cannot be responsible (Table 7). Furthermore, the sulfonium salt (**2**) did not undergo any racemization even under keeping at 61.5 °C for 1 h.

Only at a somewhat higher temperature (80.1°C,1 h), it decomposed completely to form the corresponding sulfoxide but no thermal racemization was observed. Another possibility is the intervention of the concurrent inversion process.

At a low temperature (−40°C), trifluoroacetamidate anion may attack the sulfur atom of the sulfonium salt (**2**) interacting with a basal ligand to offer the sulfilimine (**3f**) of only the retained configuration (stereoselectivity is over 94%), and at a higher temperature (22°C), the ratio (*R/S*) of retention to inversion path decreased to roughly 75 : 25.

This result suggests that the substitution with retention of configuration is more sensitive to the effect of temperature than that with inversion. This would mean that the substitution with retention proceeds through a more rigid transition state than



Scheme 4.

Table 6. Temperature effect on reaction path

T/°C	Yield/%	$[\alpha]_D$/° (*c*, $CHCl_3$)	e.e./%	Ratio of (ret/inv)
−40	47	+35.5 (1.06)	47.2	97 : 3
+4	50	+20.6 (1.02)	27.0	77 : 23
+20	23	+19.3 (1.07)	25.1	75 : 25

Table 7. Thermal change on R/S ratio of *l*-menthyloxysulfonium perchlorate (**2**)

Temp/°C	R_S-R_C/S_S-R_C[a)]
−30±2	75/25
0±2	75/25
+20±2	75/25

a) Diastereomer ratio was determined by ^1H NMR in $CDCl_3$.

the inversion process. Indeed the plots of *R/S* ratio against the reaction temperature, gave a value of energy difference between the retention and the inversion process for trifluoroacetamidate anion as $\Delta\Delta G^{\ddagger}$=4.9 KJ mol^{-1} (Fig. 5).

Mechanism. It has become quite clear from all the observations that the retention process is the main path of the nucleophilic substitution when the nucleophile used is the amidate anion bearing an acidic proton, and proceeds through a more rigid transition state than the inversion process. The most plausible mechanism for this process is as shown in Fig. 6. When *t*-butyl hypochlorite is added to an equimolar mixture of *l*-menthol and *o*-methoxyphenyl (or *o*-methylphenyl) phenyl sulfide, the corresponding *l*-menthyloxysulfonium ion is obtained. This sulfonium ion is a mixture of two diastereomers, *i.e.*, R_S—R_C and S_S—R_C, however in excess of the kinetically favored R_S—R_C conformer. When the ordinary amidate anion such as *p*-toluenesulfonamiate, benzamidate, or chloroacetamidate, attacks the sulfur atom along an apical direction, *i.e.*, the back side of the leaving group, namely *l*-menthyloxy group of the sulfonium ion at another apical direction, the reaction proceeds *via* formation of a σ-sulfurane as the key intermediate, in which both attacking and leaving groups are placed

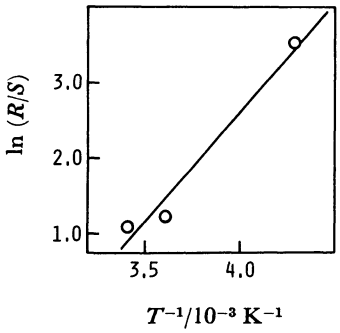


Fig. 5. The retention/inversion plots against the reaction temperature.

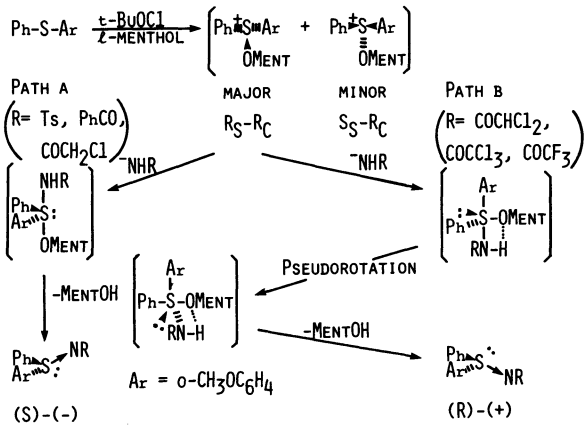


Fig. 6. Reaction mechanisms.

at apical-apical positions respectively, to result in the formation of the sulfilimine of inverted configuration on the sulfur, (path a). However, when the amidate anion, which has an acidic proton such as in dichloro, trichloro-, or trifluoroacetamidate anion, attacks the sulfur atom along an apical direction, there would be a substantial interaction between the amidate and the leaving group, *i.e.*, *l*-menthyloxy group of the sulfonium ion, and even during and after pseudorotation, the interaction would hold both groups at nearly perpendicular around the sulfur atom till the final release of *l*-menthyloxy group from the apical direction.

Thus the retention of configuration on the sulfur is resulted. This study has thus revealed that hydrogen bonding plays an important part in fixing the geometry of the entering nucleophile and the leaving group in the incipiently formed σ-sulfurane and leads the nucleophilic substitution on tricoordinate sulfur to proceed with retention of configuration.

Experimental

General. All melting points were uncorrected. IR spectra were recorded on a JASCO A-3 spectrometer. ^{1}H NMR spectra were recorded on a Hitachi Perkin-Elmer R-20 and R-600 spectrometers. Optical rotations were measured by a JASCO DIP-140 spectrometer. Circular dichroism spectra were recorded on a JASCO J-20 spectrometer.

Elemental analyses were carried out at the Chemical Analysis Center of this University.

Sulfides. The sulfides were prepared by decomposition of the diazonium salt of *o*-substituted anilines in the presence of thiophenol, as described previously.[16] Their boiling points were 146 °C (399 Pa) for *o*-methoxyphenyl sulfide (lit,[11a] 130—135 °C (266 Pa)) and 117—118 °C (399 Pa) for *o*-methylphenyl phenyl sulfide (lit,[11a] 120—125 °C (266 Pa)).

t-*Butyl Hypochlorite.* *t*-Butyl hypochlorite was prepared by chlorination of *t*-butyl alcohol by aqueous sodium hypochlorite in the presence of acetic acid as described before.[17]

(R)-(+)-S-(o-Methoxyphenyl)-S-phenyl-N-(trifluoroacetyl)-sulfilimine (3f). A mixture of *o*-methoxyphenyl phenyl sulfide (0.66 g, 3.05 mmol), *l*-menthol (0.559 g, 3.58 mmol), and dry pyridine (0.227 g, 3.50 mmol) was dissolved in 20 ml of dry acetonitrile. Into the well-stirred solution kept at −40 °C, at first *t*-butyl hypochlorite (0.388 g, 3.57 mmol) in 4 ml of dry acetonitrile and then sodium trifluoroacetamidate (prepared by treating trifluoroacetamide (0.511 g, 4.52 mmol) with 60% sodium hydride (0.18 g, 4.51 mmol)) was added. After the whole mixture was strirred at the temperature for 2 h, it was warmed up to room temperature.

Then into the reaction mixture was added aqueous dil. $Na_2S_2O_3$ and the aqueous solution was extracted with chloroform.

The residue was chromatographed on silica gel by elution with hexane–ethyl acetate (7:3). Yield was 0.527 g (53%); colorless crystals; mp 109—114 °C; $[\alpha]_D^{20}$=+35.4° ($CHCl_3$, c=1.06). The enantiomeric excess of the sulfilimine was determined by NMR using Eu(hfc) as shift reagent to be 47±5%; IR (KBr) 1630 (C=O); ^{1}H NMR ($CDCl_3$) δ=3.83 (3H,s,*o*-CH_3O–), 6.8—8.2 (9H,m, aromatic protons); Found; C, 54.45; H, 3.65; N, 4.24%. Calcd for $C_{15}H_{12}F_3NO_2S$; C, 55.04; H, 3.70; N, 4.28%.

Other optically active sulfilimines (**3a—h**) were obtained by the same procedure as described above.

(S)-(−)-S-(o-Methoxyphenyl)-S-phenyl-N-tosylsulfilimine (3a). Optically active **3a** was prepared by a similar method as described above except for using sodium *p*-toluenesulfonamidate (prepared by treating *p*-toluenesulfonamide with sodium methoxide and recrystallized from ethanol-methanol) instead of sodium trifluoroacetamidate. Yield was 47%; colorless crystals; mp 156—158 °C; $[\alpha]_D^{20}$=−40° C ($CHCl_3$, c=1.00); 41% o.p.;[11a] IR (KBr), 995(S-N); ^{1}H NMR ($CDCl_3$) δ=2.32 (3H, *p*-CH_3–), 3.70 (3H,s,*o*-CH_3O–), 6.78-8.20 (13H,m, aromatic protons).

(S)-(−)-S-(o-Methoxyphenyl)-S-phenyl-N-benzoylsulfilimine (3b). Yield was 40%; colorless crystals; mp 115.5—118 °C; $[\alpha]_D^{25}$=−17° ($CHCl_3$, c=1.03); 27±5% e.e; IR (KBr), 1590 (C=O); ^{1}H NMR ($CDCl_3$) δ=3.80 (3H,s,*o*-CH_3O–), 6.82—8.47 (14H,m, aromatic protons).

(S)-(−)-S-(o-Methoxyphenyl)-S-phenyl-N-(chloroacetyl)sulfilimine (3c). Yield was 47%; colorless crystals; mp 122—125 °C; $[\alpha]_D^{20}$=−45.5° ($CHCl_3$, c=0.994); 35±5% e.e; IR (KBr), 1590 (C=O); ^{1}H NMR ($CDCl_3$) δ=3.88 (3H,s,*o*-CH_3O–), 4.24 (2H,s,$ClCH_2$–), 6.84—8.13 (9H,m, aromatic protons); Found; C, 58.48; H, 4.49; N, 4.51%. Calcd for $C_{15}H_{14}ClNO_2S$; C, 58.53; H, 4.58; N, 4.55%.

(R)-(+)-S-(o-Methoxyphenyl)-S-phenyl-N-(dichloroacetyl)-sulfilimine (3d). Yield was 34%; colorless crystals; mp 116.5—120 °C; $[\alpha]_D^{20}$=−11.7° ($CHCl_3$, c=3.78 (3H, s,*o*-IR (KBr) 1600 (C=O); ^{1}H NMR ($CDCl_3$) δ=3.78 (3H,s,*o*-CH_3O–), 6.25 (1H,s,Cl_2CH–), 6.83—8.17 (9H,m, aromatic protons); Found; C, 52.60; H, 3.78; N, 4.09%. Calcd for $C_{15}H_{13}Cl_2NO_2S$; C, 52.64; H, 3.82; N, 4.09%.

(R)-(+)-S-(o-Methoxyphenyl)-S-phenyl-N-(trichloroacetyl) sulfilimine (3e). Yield was 72%; colorless crystals; mp 121—122 °C; $[\alpha]_D^{20}$=+26.4° ($CHCl_3$, c=0.85); 47±5% e.e.; IR (KBr) 1625 (C=O); ^{1}H NMR ($CDCl_3$) δ=3.90 (3H,s,*o*-CH_3O–), 6.85—8.23 (9H,m, aromatic protons); Found; C, 47.80; H, 3.14; N. 3.77%. Calcd for $C_{15}H_{12}Cl_3NO_2S$; C, 47.82; H, 3.21; N, 3.71%.

(S)-(−)-S-(o-Methylphenyl)-S-phenyl-N-tosylsulfilimine (3g). Yield was 72% (2.8 ml of *N,N*-dimethylformamide was added to 28 ml of acetonitrile solution as reaction solvent); colorless crystals; mp 102—103 °C; $[\alpha]_D^{25}$=−14.4° ($CHCl_3$, c=2.07); 35%o.p.[11a]; IR (KBr), 955 (S-N); ^{1}H NMR ($CDCl_3$) δ=2.36 (6H,s,*o*-CH_3– and *p*-CH_3–), 7.02—8.04 (13H,m, aromatic protons)

(R)-(+)-S-(o-Methylphenyl)-S-phenyl-N-(trifluoroacetyl) sulfilimine (3h). Yield was 96%; colorless crystals; mp 64—65°C; $[\alpha]_D^{25}$=+21° ($CHCl_3$, c=1.32); 26±5%e.e.; IR (KBr), 1640 (C=O); ^{1}H NMR ($CDCl_3$) δ=2.66 (3H,s,*o*-CH_3O–), 7.25—8.04 (9H,m, aromatic protons); Found; C, 57.91; H, 3.92; N, 4.46%. Calcd for $C_{15}H_{12}F_3NOS$; C, 57.87; H, 3.88; N, 4.49%.

Circular Dichroism Spectra. CD spectra shown in Fig. 3a, 3b, and 3c were all recorded in methanol solution.

Sulfilimines of which CD spectra were measured, have following optical rotations. (**3a**), $[\alpha]_D^{20}$=−25.5° ($CHCl_3$)

c=1.19); (**3b**), $[\alpha]_D^{20}$=−17.3° ($CHCl_3$, c=1.03); (**3c**), $[\alpha]_D^{20}$=−43.6° ($CHCl_3$, c=2.34); (**3d**), $[\alpha]_D^{20}$=+4.8° ($CHCl_3$, c=2.34); (**3e**), $[\alpha]_D^{20}$=+26.4° ($CHCl_3$, c=0.85); (**3f**), $[\alpha]_D^{20}$=+35.4° ($CHCl_3$, c=1.06); (**3g**), $[\alpha]_D^{25}$=−14.4° ($CHCl_3$, c=2.07); (**3h**), $[\alpha]_D^{25}$=+20.9° ($CHCl_3$, c=1.32).

Syntheses of Authentic Samples. (S)-(−)-S-(o-Methoxyphenyl)-S-phenyl-N-(trifluoroacetyl)sulfilimine (3f) from (S)-(−)-S-(o-Methoxyphenyl)-S-phenylsulfilimine. To a benzene solution (10 ml) of (*S*)-(−)-*S*-(*o*-methoxyphenyl)-*S*-phenylsulfilimine[11a] $[\alpha]_D^{25}$=−187° (96%o.p) (0.253 g 1.09 mmol) and dry pyridine (0.088 g, 1.12 mmol) stirred in an ice bath, trifluoroacetic anhydride (0.258 g, 1.23 mmol) was added slowly. After stirring the mixture for 1 h, the solution was washed with 10% aqueous NaOH, water, dried ($MgSO_4$), and evaporated under vacuum. The remained oily product was chromatographed on silica gel eluted with benzene: ethyl acetate=2 : 1. Yield was 0.263 g (75%); colorless oil; $[\alpha]_D^{25}$=−13.1° ($CHCl_3$, c=1.02). The IR spectrum and the ^1H NMR spectrum are identical to those of the sulfilimine obtained previously.

Other authentic sulfilimines were obtained by similar methods as described above. The acylating reagents and the results are summarized in Table 2.

(1-Methyloxy)(o-methoxyphenyl)phenylsulfonium perchlorate (2). A mixture of *o*-methoxyphenyl phenyl sulfide (0.228 g, 1.05 mmol) and *l*-menthol (0.194 g, 1.24 mmol) was dissolved in 25 ml of dry acetonitrile. Into the well-stirred solution kept at −40°C, at first *t*-butyl hypochlorite (0.125 ml, 1.05 mmol) and then silver perchlorate (0.228 g, 1.10 mmol) were added. After colorless precipitates (silver chloride) appeared, $Na_2S_2O_3$ and water were added and the solution was filterd. The filterate extracted with chloroform, was washed with water, dried ($MgSO_4$). The chloroform solution was poured into a large amount of ether. Oily product was precipitated and the ethereal layer was removed by decantation. After reprecipitation several times, the oily product was evaporated under reduced pressure. Yield was 0.153 g (31%); colorless oil; R_S-R_C: S_S-R_C=75:25. IR (NaCl), 1070 (ClO_4); ^1H NMR ($CDCl_3$) δ=0.46—2.00 (m, menthyl group protons), 3.93 (s,*o*-CH_3O-(R_S-R_C)), 4.01 (s,*o*-CH_3O-(S_S-R_C)), 6.92—8.15 (m, aromatic protons); Found; C, 58.65; H, 6.74%. Calcd for $C_{23}H_{31}ClO_6S$; C, 58.65; H, 6.63%.

Reactions of Sodium Amides with (1-Methyloxy)(o-methoxyphenyl)phenylsulfonium Perchlorate (2). Typical procedure is as following: The sulfonium salt (**2**) (0.239 g, 0.506 mmol) (*R*/*S*=83/17) was dissolved in 10 ml of dry acetonitrile and strirred at −35 °C. Into the well-stirred solution, sodium trichloroacetamidate (prepared from trichloroacetamide (0.168 g, 1.04 mmol) and 60% sodium hydride (0.041 g, 1.03 mmol)) was added at the temperature. After stirring for 20 min, water was added and extracted with chloroform. The extract was dried and evaporated under vacuum. The oily product was chromatographed on silica gel by elution with benzene–ethyl acetate (2:1). Yield was 0.028 g (39%); colorless crystals; $[\alpha]_D^{19}$=+16° ($CHCl_3$, c=1.1); 44%e.e.; 66% optical yield. The IR and the ^1H NMR spectra of sulfilimines obtained by above method are identical to those of the sulfilimines obtained previously.

Temperature Effect. A mixture of *o*-methoxyphenyl phenyl sulfide (0.215 g, 0.993 mmol) and *l*-menthol (0.195 g, 1.25 mmol) was dissolved in dry acetonitrile (15 ml).

Into the well-stirred solution kept at −40 °C, *t*-butyl hypochlorite (0.125 ml, 1.05 mmol) was added. The reaction mixture was allowed to be set at a certain temperature (−40°, +2, or +22 °C) and then sodium trifluoroacetamidate (prepared as described before) was added. Further work up procedure was the same as described before.

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