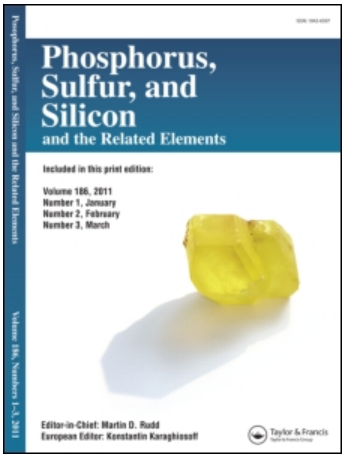

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NUCLEOPHILIC SUBSTITUTION AT TRICOORDINATE SULFUR. HYDROLYSIS OF *N*-DIARYLSULFONIODIMETHYL-SULFOXIMINIUM SALT IN BASIC AQUEOUS ACETONITRILE

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NUCLEOPHILIC SUBSTITUTION AT TRICOORDINATE SULFUR. HYDROLYSIS OF *N*-DIARYLSULFONIODIMETHYL-SULFOXIMINIUM SALT IN BASIC AQUEOUS ACETONITRILE

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N-Diarylsulfoniodimethylsulfoximinium salts (Ar_2S^+-$NS(O)Me_2X^-$), prepared by treating diaryl sulfides with *N*-halodimethylsulfoximines, were found to be hydrolyzed readily under alkaline conditions to form the corresponding diaryl sulfoxides and dimethylsulfoximine quantitatively. The reaction was found to proceed with inversion of configuration. The kinetic study of the reaction in aqueous acetonitrile was carried out and the reaction was found to follow the second-order rate equation, namely, first-order each in the sulfoniosulfoximinium salt and the base, respectively. Activation parameters, determined for the reaction with *N*-diphenylsulfoniodimethylsulfoximinium perchlorate were found to be $\Delta H^{\ddagger} = 12.2$ Kcal · mol^{-1}, $\Delta S^{\ddagger} = -17.0$ eu. The rate constants of the hydrolyses for the ring-substituted derivatives gave a good correlation with the Hammett's σ constants and gave a ρ value of 3.08. This large ρ value suggests that the reaction involves the formation of the sulfurane intermediate at the rate-determining step of the reaction.

INTRODUCTION

Nucleophilic substitution on the tricoordinate sulfur atom has received much attention in recent years by those who are interested in the mechanistic investigation of organic sulfur chemistry.[1] One of the most fascinating problems in these reactions is whether the reaction proceeds through an S_N2 type mechanistic path, in which both bond breaking and bond making take place in a concerted but nonsynchronous manner, or the reaction is a stepwise process, namely, involving addition–elimination (A–E) *via* formation of a tetracoordinate sulfurane as an intermediate. Many accumulated experimental data appear to be consistent with the mechanism that does not require the incipient formation of a sulfurane intermediate. The following observations are representative of the data: (1) a large steric effect of retardation by bulky substituents in the reaction of thiosulfates with sulfite ion,[2] (2) the complete inversion of configuration in the reaction of several optically active tricoordinate sulfur compounds with nucleophiles,[3] and (3) the lack of ^{18}O incorporation during

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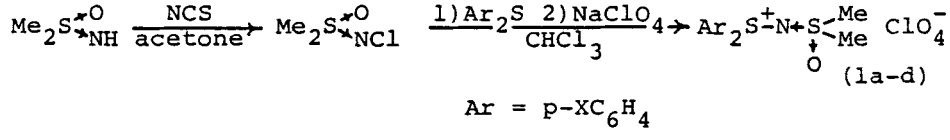
the alkaline hydrolysis of sulfonates or sulfites.[4] These observations seem to rule out the formation of the relatively stable tetracoordinate intermediate which is generally formed in the alkaline hydrolysis of carboxylic esters. Therefore, nucleophilic substitution on the tricoordinate sulfur has been believed to proceed *via* a direct S_N2 type displacement. However, there is a possibility that the incipiently formed intermediate is too unstable to be detected. The markedly large acceleration of the rate of alkaline hydrolysis of aryl p-substituted benzenethiolsulfonates[5] and *p*-substituted benzenesulfonates[6,7] by electron-withdrawing para substituents does indicate that the initial nucleophilic attack of hydroxide ion on the tri- or tetracoordinate sulfur atom controls the rate of the alkaline hydrolyses of these esters. This means that the cleavage of the thiophenolate or the phenolate in these hydrolyses is quite fast and does not require any extra activation energy. In these reactions, in which the initial nucleophilic attack on the positively charged sulfur atom is the rate-determining step whereas the subsequent heterolysis of the leaving group is fast and hence requires less energy than that for the initial step, it is not easy to detect the incipiently formed σ-sulfurane intermediate. Only kinetic experiments may indicate that the rate is accelerated markedly by substitution of an electron-withdrawing group either at the adjacent position or at the position conjugated to the reacting sulfur atom. Therefore, the question has always remained whether the hydrolysis involves the incipient formation of a σ-sulfurane intermediate in nucleophilic substitution on the tri- and tetracoordinate sulfur atom.

Many sulfonium salts have been used as important reagents for various organic syntheses.[8] For examples, the Pummerer reaction,[9] the Kornblum oxidation,[10] the Corey–Kim oxidation,[11] and the Sommelet–Houser type rearrangement[12] are only a few examples of useful synthetic reactions. In any of these reactions, heterosulfonium salts are considered to be the essential intermediates. Numerous stereochemical studies on the nucleophilic substitutions of heterosulfonium salts have been carried out by us[13] and others.[14–16] However, there has been no kinetic study on the nucleophilic substitution of *N*-sulfoniosulfoximinium derivatives. We have now investigated the kinetic behavior of *N*-sulfoniosulfoximinium salts in alkaline hydrolysis in order to compare the mode of the reaction with those of other tricoordinate sulfur derivatives.

RESULTS AND DISCUSSION

Product

N-Diarylsulfoniodimethylsulfoximinium perchlorates (**1a–d**) were obtained by treating diaryl sulfides first with *N*-chlorodimethylsulfoximine, followed by addition of excess $NaClO_4$ as shown in Scheme 1.[17] Yields and some spectral data are summarized on Table I. In the alkaline hydrolysis of *N*-sulfoniosulfoximinium salts, two



SCHEME 1

TABLE I

Yields, elemental analyses, and spectral data of *N*-diarylsulfoniodimethylsulfoximinium perchlorate (**1a–d**)

	X	Yield (%)	mp (°C)	C	H	N		^{1}H NMR ($CDCl_3$) (ppm)	IR (cm^{-1})
1a	H	27	182–183	44.41	4.27	3.53	(Found)	3.65 (6 H, s, Me)	1085, 1105
				44.50	4.26	3.70	(Calcd)	7.40–8.37 (10 H, m, arom)	980, 1120
1b	Cl	29	138–141	37.50	3.17	3.12	(Found)	3.64 (6 H, s, Me)	1085, 1040
				37.63	3.15	3.13	(Calcd)	7.56, 7.90 (8 H, dd, J = 10 Hz, arom)	1118, 1145
1c	Me	39	104–105	47.27	5.00	3.46	(Found)	2.42 (6 H, s, p-Me), 3.59 (6 H, s, Me)	1085, 1118
				47.34	4.96	3.45	(Calcd)	7.40, 7.73 (8 H, dd, J = 8 Hz, arom)	1220, 985
1d	OMe	27	oil	43.59	4.51	3.10	(Found)	3.57 (6 H, s, Me), 3.86 (6 H, s, p-MeO)	1085, 1590
				43.88	4.60	3.19	(Calcd)	7.09, 7.76 (8 H, dd, J = 9 Hz, arom)	1030, 1260

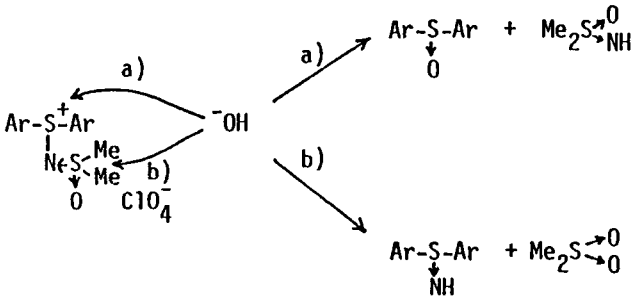
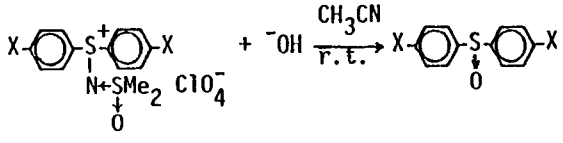


FIGURE 1 Two attacking sites for nucleophilic substitution.

different products are considered to be formed depending upon the site of the nucleophilic attack of hydroxide ion, since the sulfonium salts have two different sulfur atom (— S— and — S—), which can be attacked by OH^- ion. Therefore, if hydroxide ion attacks the sulfilimino sulfur (path a), diaryl sulfoxide and dimethylsulfoximine should be obtained; whereas if the attacking site of hydroxide ion would be the sulfoximino sulfur (path b), diaryl sulfilimine and dimethyl sulfone are expected to be the major products (Figure 1). Actually, in the alkaline hydrolyses of *N*-diarylsulfoniodimethylsulfoximinium perchlorates (**1a–d**), the corresponding diaryl sulfoxides were obtained quantitatively (Table II), demonstrating clearly that hydroxide ion attacks solely on the sulfilimino sulfur atom (path a).[18] The results are shown in Table II.

TABLE II

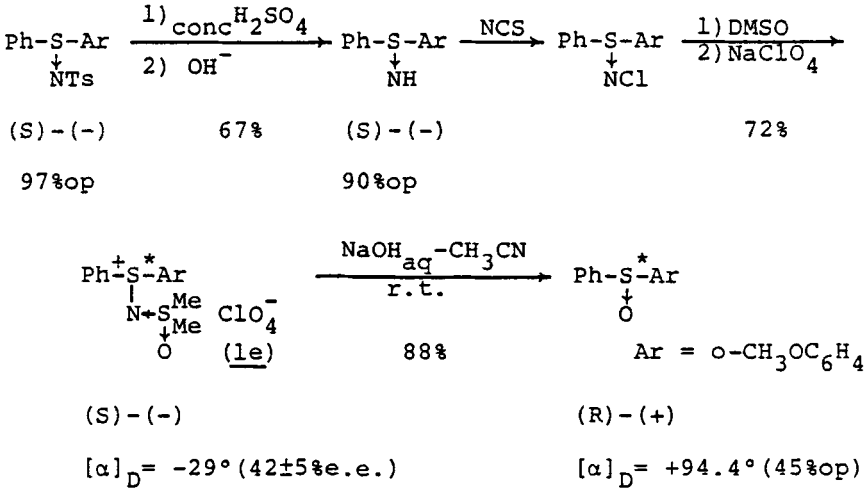
Yields of sulfoxides as products for alkaline hydrolyses of salts (**1a–d**)



X	Yield (%)	mp (°C)
Cl	98	144.5–146.5
H	> 98	71.0–72.0
Me	95	95.5–96.5
OMe	97	93.5–94.0

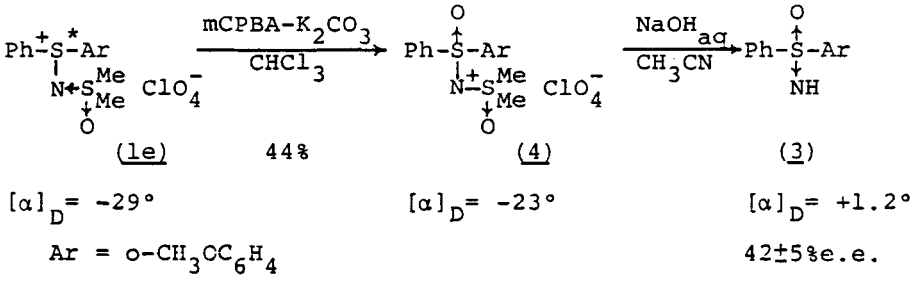
Stereochemistry

Stereochemistry for this alkaline hydrolysis was studied using optically active *N*-*o*-methoxyphenylphenylsulfoniodimethylsulfoximinium perchlorate (**1e**). Optically active sulfoximinium salt (**1e**) was prepared from optically active *o*-methoxyphenylphenyl-*N*-*p*-tosylsulfilimine as shown in Scheme 2. In order to determine the



SCHEME 2

absolute configuration and the enantiomeric excess of the sulfoximinium salt (**1e**), it was converted to *o*-methoxyphenyl-phenyl-sulfoximine (**3**) of which the absolute configuration and the optical rotation, *i.e.*, R; $[\alpha]_D$ (max.) = 2.4° are known, as shown in Scheme 3. From the measurement of the optical rotation of the sulfoximine (**3**), $[\alpha]_D^{20} = +1.2°$ ($CHCl_3$, c = 3.16), the absolute configuration of the sulfoximine (**3**) was confirmed to be R. Furthermore, based on the NMR study using Eu(tfc) as a shift reagent, the enantiomeric excess of the sulfoximine (**3**) was found to be 42 ± 5%. Since both the oxidation of the sulfoximinium salt (**1e**) and the hydrolysis of the S-oxidized compound (**4**) proceeded with retention of configuration on the sulfonio sulfur atom, the sulfoximinium salt (**1e**) which had an optical rotation of −29° ($CHCl_3$, c = 1.334), was determined to be 42 ± 5% e.e. and hence had the S configuration. The salt (**1e**) was hydrolyzed with 10% aqueous NaOH in acetonitrile to form the corresponding optically active *o*-methoxyphenyl phenyl sulfoxide having $[\alpha]_D^{20} = 94°$ ($CHCl_3$, c = 1.1). Upon comparison of the absolute configuration and the e.e. value of the same sulfoxide in the literature,[19] the sulfoxide thus obtained had 45% optical purity, with the R configuration. Therefore, the alkaline hydrolysis of the sulfoximinium salt (**1e**) proceeded with complete (over 98%) inversion of configuration.



SCHEME 3

TABLE III

Second-order rate constants for various temperature

Temp. (°C)	k_2 ($l \cdot M^{-1} \cdot sec^{-1}$)
50.0	6.58
40.2	3.93
30.0	1.88
20.0	0.897

$E_a = 12.8 \pm 0.1$ Kcal · mol^{-1}.
$\Delta H^{\ddagger}$ (30.0°C) = 12.2 ± 0.5 Kcal · mol^{-1},
$\Delta S^{\ddagger}$ (30.0°C) = −17.0 ± 0.7 eu.

Kinetics

A kinetic investigation of the alkaline hydrolysis of *N*-diphenylsulfoniodimethylsulfoximinium perchlorate was carried out at various temperatures by the rapid conductometric method.[20] The rates were found to follow the second-order equation. The second-order rate constants k_2 ($l \cdot M^{-1} \cdot sec^{-1}$) thus obtained at several temperatures are summarized in Table III, and a typical example of a second-order plot against time is shown in Figure 2. The rate constant obtained for (**1a**) is 1.88 $l \cdot M^{-1} \cdot sec^{-1}$ at 30.0°C. From the Arrehenius plot shown in Table IV, both energy and entropy of activation for the hydrolysis were calculated to be 12.8 Kcal · mol^{-1} and −17.0 eu (30.0°C), respectively for (**1a**). In order to find the polar effect of substituents on this hydrolysis of the sulfonium salt, kinetic measurements were also carried out with several *p*-substituted diarylsulfonium salts. The results are shown in Table IV. Inspection of the results reveals that the rate is accelerated by introduction of any electron-withdrawing group into the para position of the aryl ring in (**1**), whereas that of an electron-donating group at the para position retarded the reaction. The Hammett's plot of the rates against σ values gave a ρ value of 3.08. (Fig. 3)

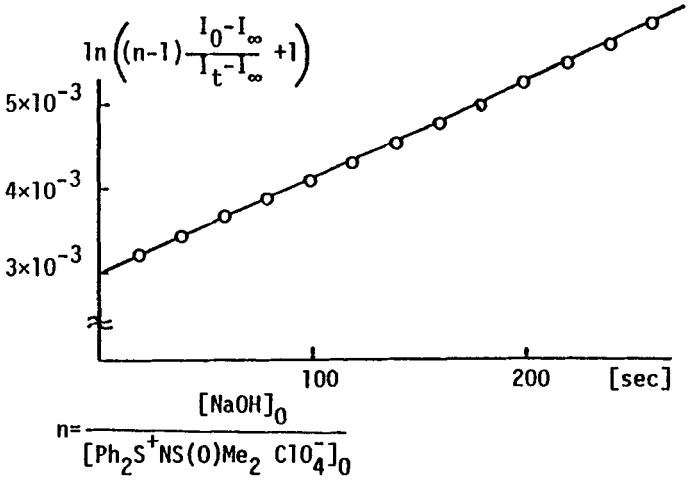


FIGURE 2 Second-order plot of alkaline hydrolysis of *N*-diphenylsulfoniodimethylsulfoximinium perchlorate (**1a**) at 30.0°C.

TABLE IV

Second-order rate constants for alkaline hydrolysis of (**1a–d**), at 30.0°C

X	k_2 ($l \cdot M^{-1} \cdot sec^{-1}$)	k_X/k_H
—Cl	8.64	4.60
—H	1.88	1
—Me	0.638	0.339
—OMe	0.417	0.222

As was expected, the hydrolysis of *N*-sulfoniosulfoximinium salt proceeded more rapidly than the similar hydrolyses of corresponding sulfoxides[21] and sulfilimines.[22] This is probably due to the weaker S—N single bond of the sulfoximinium salt (**1**) than the normal S—O or S—N semipolar bond in ordinary sulfoxides or sulfilimines. Both the stereochemistry and the kinetic data obtained in the present investigation, namely, the second-order reaction rate, the similar $\Delta S^{\ddagger}$ value to that in the acid-catalyzed hydrolysis of the sulfilimine[22a] and also the facile acid-catalyzed racemization of the optically active sulfoxide,[21] appear to suggest that the alkaline hydrolysis of the salt (**1**) proceeds through an S_N2 type process in which hydroxide ion attacks the sulfur atom from the back side of the leaving group.

Ciuffarin *et al.* have reported a rather large ρ value ($\rho = 2.8$) in the alkaline hydrolysis of the substituted benzenesulfonyl fluoride.[23] They suggested that if the reaction proceeded *via* an S_N2 type mechanism which does not require the accumulation of a negative charge on the central sulfur atom, a small ρ value would be obtained, but a large positive ρ value should be obtained in the reaction involving

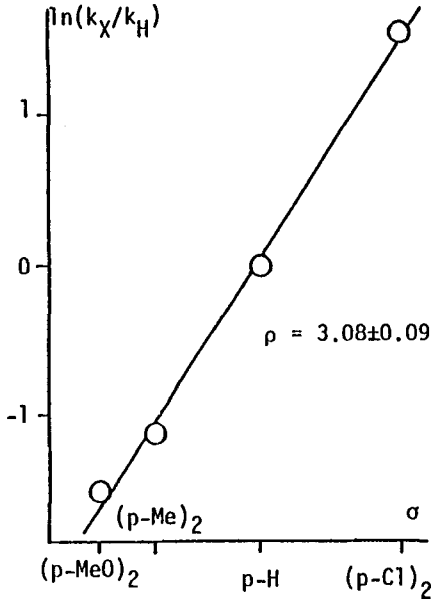


FIGURE 3 Hammett plot for alkaline hydrolysis of (**1a–d**).

the formation of a σ-sulfurane as an intermediate. In such a reaction, bond forming is considered to progress far more than bond breaking and the negative charge should be concentrated on the central sulfur atom at the transition state. In the alkaline hydrolyses of mesityl arenesulfinamide,[24] phenyl arenesulfonate,[7c] and aryl arenethiolsulfinate,[5] large polar substituent effects were reported; namely, $\rho = +1.3$ (the alkaline hydrolysis of mesityl arenesulfinamide), $\rho = +2.2$ (phenyl arenesulfonate), and $\rho = +1.6$ (aryl arenethiolsulfinate). However, in any case of these alkaline hydrolyses, no significant ^{18}O incorporation was observed during the hydrolysis in ^{18}O-enriched water.[4b,24] Further, in the reaction of aryl-methyl-*N*-*p*-tosylsulfilimine with triphenylphosphine, which was presumed to involve the incipient formation of a sulfurane as an intermediate, a large positive ρ value (3.7) was observed. Thus the large ρ value does actually seem to mean the possible formation of a sulfurane as suggested by Ciuffarin *et al.* If the σ-sulfurane formed would collapse so fast, there is no possibility of ^{18}O incorporation into the starting sulfonate esters. Thus the unusually large positive ρ value (+3.08) observed in these experiments seems to support the formation of a σ-sulfurane as an incipient intermediate.

EXPERIMENTAL

IR spectra were recorded on a JASCO A-3. NMR spectra were recorded on a Hitachi Perkin-Elmer R-600. Melting points were uncorrected. Electric conductivities were measured by a Taiyo-sha 76A-811L.

Sulfides. The sulfides were prepared by decomposition of diazonium salts of *p*-substituted anilines in the presence of *p*-substituted benzenethiols, as described before.[25] Di-*p*-chlorophenyl sulfide, 95–96°C (mp). Di-*p*-methylphenyl sulfide, 141°C/4 mmHg (bp). Di-*p*-methoxyphenyl sulfide, 43–45°C (mp).

N-Chlorodimethylsulfoximine. The acetone solution (45 ml) of dimethylsulfoximine[26] (2.55 g, 27.4 mmol) was stirred in an ice bath and into this solution *N*-chlorosuccinimide (3.66 g, 27.4 mmol) was added. After 24 h, the acetone solution was evaporated and the residual oil was chromatographed on silica gel eluted first with ethylacetate, and then with chloroform. The chloroform solution was evaporated under vacuum and the oily product remained. Yield, 2.37 g (67%).

N-Diphenylsulfoniodimethylsulfoximinium perchlorate (**1a**). To a stirred chloroform solution (20 ml) of *N*-chlorodimethylsulfoximine (0.828 g, 6.49 mmol), phenyl sulfide, (1.21 g, 6.49 mmol) was added at room temperature and the whole solution was stirred overnight. To the solution, excess $NaClO_4$ was added and the solution was continued to stir for 24 h. The chloroform solution was washed with water, dried over $MgSO_4$ (anhydrous), and evaporated under vacuum. Crystals obtained were recrystallized from ethanol–hexane. Yield, 1.10 g (45%). Colorless crystals; mp, 182–183°C; IR (KBr) 1185, 1120, 1105, and 980 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 3.65$ (6 H, s, $-NS(O)Me_2$), 7.40–8.37 (10 H, m, aromatic protons); Found: C, 44.41; H, 4.27; N, 3.53%. Calcd. for $C_{14}H_{16}ClNO_5S_2$: C, 44.80; H, 4.26; N, 3.70%. Other N-diarylsulfoniodimethylsulfoximinium perchlorates (**1b–d**) were prepared similarly.

N-Di-p-chlorobenzenesulfoniodimethylsulfoximinium perchlorate (**1b**). Yield was 29%. Colorless crystals; mp 139–140°C; IR (KBr) 1145, 1118, 1085, and 1040 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 3.64$ (6 H, s, $-NS(O)Me_2$), 7.56, 7.90 (8 H, dd, $J = 10$ Hz, aromatic protons); Found: C, 37.50; H, 3.17; N, 3.12%. Calcd. for $C_{14}H_{14}Cl_3NO_5S_2$: C, 37.63; H, 3.15; N, 3.13%.

N-Di-p-methylbenzenesulfoniodimethylsulfoximinium perchlorate (**1c**). Yield was 39%. Colorless crystals; mp, 104–105°C; IR (KBr) 1220, 1118, 1085, and 985 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 2.42$ (6 H, s, p-CH_3—), 3.59 (6 H, s, $-NS(O)Me_2$), 7.40, 7.73 (8 H, dd, $J = 8$ Hz, aromatic protons); Found: C, 47.27; H, 5.00; N, 3.46%. Calcd. for $C_{16}H_{20}ClNO_5S_2$: C, 47.34; H, 4.96; N, 3.45%.

N-Di-p-methoxybenzenesulfoniodimethylsulfoximinium perchlorate (**1d**). Yield was 21%. Colorless oil; IR (NaCl) 1590, 1260, 1085, and 1030 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 3.57$ (6 H, s, $-NS(O)Me_2$), 3.86 (6 H, s, p-CH_3O—), 7.09, 7.76 (8 H, dd, $J = 9$ Hz, aromatic protons); Found: C, 43.59; H, 4.51; N, 3.10%. Calcd. for $C_{16}H_{20}ClNO_7S_2$: C, 43.88; H, 4.60; N, 3.19%.

Optically active N-o-methoxyphenylphenylsulfoniodimethylsulfoximinium perchlorate (**1e**). Optically active *o*-methoxyphenylphenylsulfilimine (**2**) (o.p. = 90%) was prepared as previously reported.[16] To an acetone solution (30 ml) of (**2**) (0.610 g, 2.64 mmol), *N*-chlorosuccinimide (0.353 g, 2.64 mmol) was added with stirring, under cooling in an ice bath for 10 min. The solution was poured onto ice water, and a colorless precipitate appeared was filtered. This precipitate (*N*-chlorosulfilimine) was dissolved in dimethyl sulfoxide and the dimethyl sulfoxide solution was stirred at room temperature. After stirring the mixture for 2 days, excess $NaClO_4$ was added and the solution was poured into ether. An oily product was obtained and ether was removed by decantation. The residue was dissolved in chloroform, washed with water, dried, and chloroform was evaporated. Yield was 0.773 g (69%). Colorless oil; $[\alpha]_D^{20} = -28.5°$ ($CHCl_3$, c = 1.33); IR (NaCl) 1485, 1230, 1085, and 1035 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.60 (6 H, s, —NS(O)Me_2), 3.92 (3 H, s, *o*-CH_3O—), 6.93–8.07 (9 H, m, aromatic protons); Found: C, 42.59; H, 4.25; N, 3.21%. Calcd. for $C_{15}H_{20}ClNO_7S_2$: C, 42.30; H, 4.72; N, 3.29%.

Determination of the absolute configuration and enantiomeric excess of (**1e**). To a chloroform solution (5 ml) of a mixture of 70% *m*-chloroperbenzoic acid (0.114 g, 0.462 mmol) and anhydrous K_2CO_3 (0.0461 g, 0.333 mmol) stirred in an ice bath for 5 min, a chloroform solution (2 ml) of (**1e**) (0.108 g, 0.264 mmol) was added. The mixture was stirred for overnight at room temperature, an excess of $NaClO_4$ was added and the mixture was kept standing for overnight. The chloroform solution was filtered and the filterate was evaporated. The remaining oily product was chromatographed on silica gel eluted first with ethylacetate, and then with ethanol. The ethanol solution was evaporated and the oily product (optically active *o*-methoxyphenylphenylsulfoximiniumdimethylsulfoximinium perchlorate (**3**)) remained. Yield was 0.55 g (44%). Colorless crystals; $[\alpha]_D^{20} = -23.1°$ ($CHCl_3$, c = 0.988); mp, 93–95°C; IR (KBr), 1480, 1280, 1250, 1230, and 1085 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.75 (6 H, s, —NS(O)Me_2), 3.82 (3 H, s, *o*-CH_3O—), 6.93–8.33 (9 H, m, aromatic protons).

To an acetonitrile solution (10 ml) of (**3**) (0.049 g, 0.12 mmol), 10% aqueous NaOH was added with stirring under cooling in an ice bath for overnight. Acetonitrile was evaporated under vacuum. The aqueous solution was extracted with chloroform, the organic solution was washed with water, dried ($MgSO_4$). After the solvent was evaporated, the crystals remained were identified to be *o*-methoxyphenylphenylsulfoximine (**4**). Yield was 0.032 g (100%). $[\alpha]_D^{20} = +1.2°$ ($CHCl_3$, c = 3.16). The enantiomeric excess of (**4**) was determined, by NMR using Eu(tfc) as shift reagent, to be 42 ± 5%.

Alkaline hydrolysis of (**1a**). To an acetonitrile solution (20 ml) of (**1a**) (0.058 g, 0.154 mmol), 10% aqueous NaOH was added and the solution was stirred for overnight. The solution was extracted with dichloromethane, and dried ($MgSO_4$), and the solvent was evaporated under vacuum. The residue was chromatographed on silica gel using carbontetrachloride : ethylacetate = 2 : 1 as an eluent. Yield was 0.031 g (100%). Colorless crystals; mp, 71–72°C. Other *N*-diarylsulfoniodimethylsulfoximinium perchlorates (**1b–d**) were hydrolyzed by the same method and the corresponding sulfoxides were isolated (Table II).

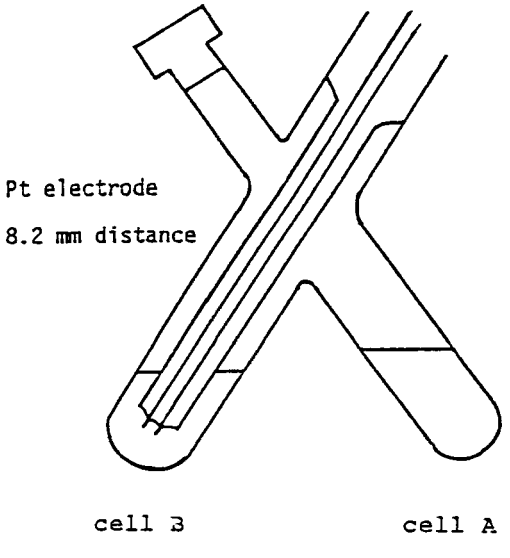


FIGURE 4 Reaction cell.

Kinetics. The conductivity cell designed for this investigation is shown in Figure 4. A typical run is as follows: 5 ml of 20% aqueous acetonitrile solution of (**1a**) (1.988×10^{-3} M) was placed in a reaction cell A and 5 ml of 20% aqueous acetonitrile solution of NaOH (2.004×10^{-3} M) was placed in a reaction cell B. The apparatus was placed in a constant temperature bath set at 30.0 ± 0.05°C and kept for about 45 min. Then the solutions of A and B were mixed and the electric current was measured and recorded under a constant voltage. Second-order rate constants (k_2) were calculated from following equation.

$$a(n-1)k_2t = \ln\left\{(n-1)\frac{I_0 - I_\infty}{I_t - I_\infty} + 1\right\} - \ln n$$

I_0: initial electric current

I_∞: final electric current

a: initial concentration of (**1a–d**)

$$n = \frac{[\text{initial concentration of base}]}{[\text{initial concentration of (1)}]}$$

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