Kinetic Study on the Alkaline Hydrolysis of *S,S*-Diaryl-*N*-halosulfilimines

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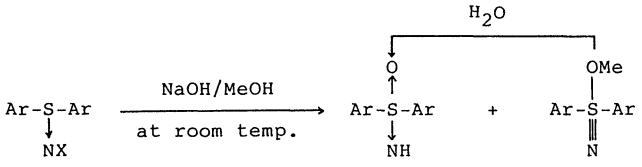
Kinetics for the alkaline hydrolysis of *S,S*-diaryl-*N*-bromosulfilimines were carried out in aqueous methanol. The observed pseudo-first-order rate constants were found to give a linear correlation with the concentration of sodium hydroxide, $k=k_1+k_2$[NaOH]. The first-order rate constants k_1 showed a large negative Hammett ρ value (−2.43) for the substituent effect on the phenyl group, nearly zero activation entropy (−0.9±13.1 $JK^{-1}mol^{-1}$) and a relatively large m value (0.638) against the solvent ionizing power Y value suggesting that the reaction process for k_1 close to S_N1. The salt effect, the deuterium solvent isotope effect and the steric effect are also in accord with the S_N1 mechanism. On the other hand, the second-order rate constants k_2 revealed a small Hammett ρ value, a negative activation entropy (−44.0±4.0 $JK^{-1}mol^{-1}$), a small m value (0.153) and a steric deceleration by ortho substituents showing that the reaction for k_2 is S_N2-like. The salt effect and the solvent isotope effect are also compatible with the S_N2-like mechanism. Meanwhile, the k_1 for *S,S*-diphenyl-*N*-halosulfilimines remarkably increased in the order of *N*-iodo<*N*-bromo<*N*-chloro. This reactivity might be due to the lone pair-lone pair repulsion at the reactant state. From these observations, the alkaline hydrolysis of *S,S*-diaryl-*N*-halosulfilimines was confirmed to proceed via concurrent two mechanisms, the S_N1-like mechanism involving nitridosulfonium cation ($>^+S{\equiv}N$) as an intermediate and the S_N2'-like mechanism with the transition state in which the N-X bond cleavage is more progressed than the S-O bond formation with nucleophiles (^-OH, ^-OMe).

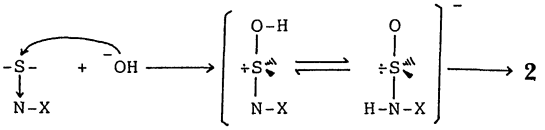
S,S-Diaryl-*N*-halosulfilimines (**1**) are useful compounds to prepare many other derivatives of sulfilimines. Reactions of **1** with various nucleophiles have been investigated since 1972.[1-4] It has been suggested that they have three reaction sites (sulfinyl sulfur, imino nitrogen, and halogen) toward nucleophiles.

Among these, the reaction of **1** with sodium hydroxide in methanol affords the corresponding *S,S*-diarylsulfoximines (**2**) quantitatively. This reaction is very useful for the preparation of **2** which generally have pharmaceutical activities, since preparation of **2** was sometimes tedious and synthesized examples of **2** were few. In spite of the convenience of this reaction, the mechanism has not yet been clarified. Recently, we found that a novel intermediate, *S,S*-diaryl-*S*-methoxythiazyne (**3**), is incipiently formed in this reaction and it is subject to further hydrolysis to give **2**[5]



1 (X=Cl, Br) **2** **3**

Therefore, it is very interesting to investigate how this reaction proceeds, because attacking site of the nucleophile(sulfinyl sulfur) is different from the atom carrying the leaving group (imino nitrogen) like S_N2' reaction. From the results of stereochemistry using optically active (−)-(*S*)-*S*-(*o*-methoxyphenyl)-*S*-phenyl-*N*-chlorosulfilimine and other observations, the reaction was suggested to proceed by a nucleophilic attack of hydroxide ion on the sulfur atom and following release of chloride ion from the imino nitrogen with retention of configuration.[4]



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However, these results are not enough to elucidate the transition state of this reaction. Therefore, in order to understand the mechanism of this reaction, a variety of *S,S*-diaryl-*N*-bromosulfilimines were prepared and subjected to the hydrolysis, and their kinetic investigations were carried out.

Results and Discussion

Kinetics. Substituent Effect and Activation Parameters. The reaction rates of the alkaline hydrolysis of *S,S*-diaryl-*N*- bromosulfilimines (**1a**) were determined by following the decrease in the UV absorption at 352 nm due to **1a**. The reaction in excess sodium hydroxide was found to follow a good pseudo-first-order kinetic equation for two half lives. The first-order rate constants obtained in MeOH and 1/1 (v/v) MeOH/H_2O were plotted against the concentration of sodium hydroxide in Fig. 1. A linear correlation was observed, $k=k_1+k_2$[NaOH]. The intercept k_1 is significant in MeOH/H_2O while it is nearly zero in MeOH. The value k_1 is the alkali-independent first-order rate constant, while the k_2 is the second-order rate constant. The kinetic data k_1 and k_2 obtained for the alkaline hydrolysis of *S,S*-diaryl-*N*-halosulfilimines (**1**) with excess sodium hydroxide in 1/1 (v/v) MeOH/H_2O are summarized in Table 1.

The substituent effect on the phenyl group (Table 1) was examined. The electron-donating group such

Table 1. Kinetic Data of the Alkaline Hydrolysis of *S,S*-Diaryl-*N*-halosulfilimines, $YC_6H_4S(\rightarrow NX)C_6H_4Z$ (**1**), in 1/1 (v/v) MeOH/H_2O

	X	Y	Z	Temp °C	$k_1\times10^4$ s^{-1}	$k_2\times10^3$ $dm^3\,mol^{-1}\,s^{-1}$	r
		H	H	30.0	2.22	2.24	0.999
		H	H	35.0	3.62	3.56	0.999
		H	H	40.0	7.33	5.92	0.998
1a	Br	H	H	50.0	23.6	15.4	0.999
		p-Me	*p*-Me	35.0	29.9	4.60	0.978
		p-Me	H	35.0	12.9	4.63	0.972
		p-Cl	H	35.0	1.49	5.13	0.999
		m-Cl	H	35.0	0.522	4.71	0.999
		o-Me	H	35.0	4.09	0.539	0.999
		o-OMe	H	35.0	4.30	0.270	0.999
1b	Cl	H	H	35.0	51.0	2.59	0.999
1c[a]	I	H	H	35.0	2.25	0.381	0.998

a) Rates for reduction.
k_1 for **1a(H,H)**: $\Delta H^{\ddagger}=(95.4\pm4.1)$ kJ mol^{-1}, $\Delta S^{\ddagger}=-(0.9\pm13.1)$ J K^{-1} mol^{-1} (35.0 °C) (r=0.998), ρ=−2.43 (r=0.996). k_2 for **1a(H,H)**: $\Delta H^{\ddagger}=(76.4\pm1.3)$ kJ mol^{-1}, $\Delta S^{\ddagger}=-(44.0\pm4.0)$ J K^{-1} mol^{-1} (35.0 °C) (r=0.999), $\rho\simeq0$.

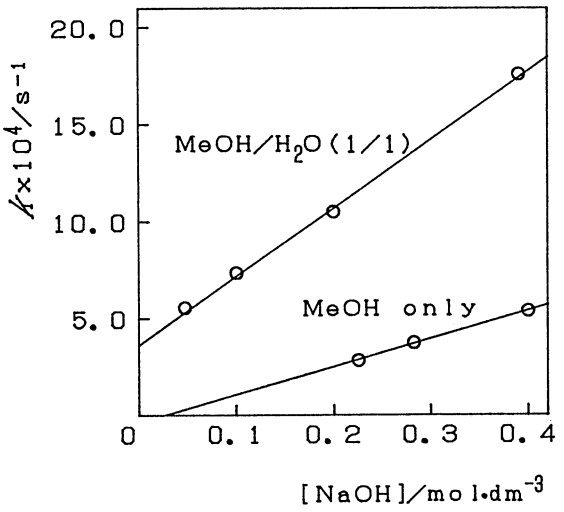


Fig. 1. Typical plots of pseudo-first-order rate constants (k) of the alkaline hydrolysis of *S,S*-diphenyl-*N*-bromosulfilimine (**1a(H,H)**) vs. the concentration of sodium hydroxide (35 °C).

as the *p*-CH_3 group accelerates the uncatalyzed reaction (k_1) to give a large negative Hammett ρ value (ρ=−2.43, r=0.996), while k_2 values are little influenced, the Hammett ρ value being nearly zero.

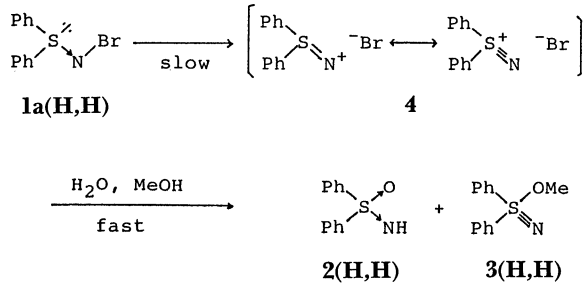
Arrhenius plot for the k_1 values in the reaction of *S,S*-diphenyl-*N*-bromosulfilimines (**1a(H,H)**) afforded an activation enthalpy 95.4 kJ mol^{-1} (35 °C) and nearly zero activation entropy (−0.9 J K^{-1} mol^{-1}, 35 °C) while the k_2 afforded an activation enthalpy 76.4 kJ mol^{-1} (35 °C) and a negative activation entropy (−44.0 J K^{-1} mol^{-1}, 35 °C).

The large negative ρ value and nearly zero activation entropy for k_1 are incompatible with usual nucleophilic substitution on the sulfinyl sulfur atom of *S*-aryl-*N*-tosylsulfilimines. For example, positive ρ values 1.19[6,7] and 1.2,[8] and relatively large negative activation entropies, i.e., −78.2—−94.5 J K^{-1} mol^{-1} and −100 J K^{-1} mol^{-1} are reported for the acidic and alkaline hydrolysis of *S*-phenyl-*S*-methyl-*N*-tosylsulfilimine, respectively. Therefore, the substituent effect and the activation parameters for the present system are in conflict with mechanism proposed previously.[4]

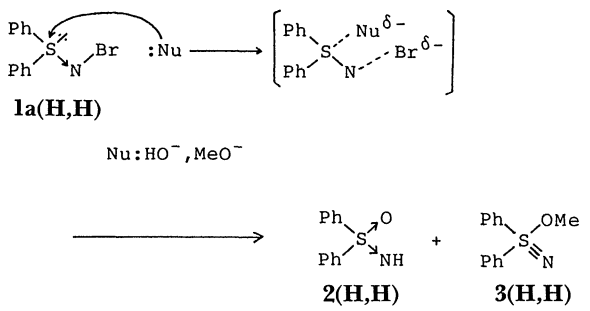
The large negative Hammett ρ value (ρ=−2.43) for k_1 indicates formation of considerable positive charge on the S(IV) atom at the transition state. Further, the large activation entropy suggests that this reaction occurs with a loose transition state. These two observations suggest that the reaction for k_1 proceeds via an S_Ni-like mechanism involving a nitridosulfonium cation[9] as an intermediate (**4** in Scheme 1).

Namely the mechanism may involve initial heterolytic cleavage of the N-Br bond to afford the cation **4** followed by the fast attack of nucleophiles (H_2O or MeOH) to afford the diphenylsulfoximine (**2(H,H)**) or the diphenylmethoxythiazyne (**3(H,H)**). The value of the activation entropy is probably a result of the cancellation of the expansion of the N-Br bond by the solvation of halide ion in the transition state.

On the other hand, the hydroxide-dependent reac-



Scheme 1.



Scheme 2.

tion for k_2 seems to involve an S_N2-like mechanism (Scheme 2) with very small substituent effect and negative activation energy.

Solvent Effect. The reaction rates k_1 and k_2 for **1a(H,H)** were measured in several composition of water-methanol mixed solvent. The rate constants k_1 and k_2 obtained are listed in Table 2. Both k_1 and k_2 were found to increase as the fraction of water increases.

Plots of the logarithms of the k_1 and k_2 vs. Y values of water-methanol,[10] ionizing power, afforded good straight lines to give the m values 0.638 for k_1 and 0.153 for k_2, respectively (Table 3). The small m value obtained for k_2 may be within the range of values for S_N2 reaction. Meanwhile, the large m value for k_1 indicates that the reaction for k_1 has a considerable S_N1-character though the m value is smaller than that for the standard solvolysis of t-butyl chloride (m=1.00)[10]

Salt Effect. Kinetics of the alkaline hydrolysis of **1a(H,H)** was carried out in the presence of lithium perchlorate in 1/1 (v/v) H_2O/CH_3OH. The rate constant k_1 was found to increase with increasing concentration of the salt, while the rate constant k_2 slightly decreases as shown in Table 4. The S_N1 reactions are usually remarkably accelerated by an addition of salt such as lithium perchlorate,[11] while S_N2 reactions of neutral substrates with ionic nucleophiles are decelerated.[12,13] Therefore the observed salt effects are also compatible with the above mechanistic conclusions.

Solvent Isotope Effect. The solvolysis of t-butyl chloride, which is considered as a standard S_N1 reaction, has been found to proceed more slowly in D_2O than in H_2O by a factor of k_H/k_D=1.4, while the

Table 2. Effects of the Concentration of NaOH on the Rate of the Alkaline Hydrolysis of *S,S*-Diphenyl-*N*-bromosulfilimine (**1a (H,H)**) in MeOH/H_2O (35.0 °C)

MeOH : H_2O	[NaOH]×10²	k×10⁴	k_1×10⁴	k_2×10³
v : v	mol dm⁻³	s⁻¹	s⁻¹	dm³ mol⁻¹ s⁻¹
1 : 2	1.81	12.0	11.0	4.53
	3.61	12.3		
	7.22	14.3		
	14.4	17.5		
1 : 1	4.97	5.40	3.62	3.56
	9.93	7.27		
	19.6	10.4		
	39.1	17.6		
2 : 1	1.81	1.84	1.35	2.74
	3.61	2.36		
	7.22	3.36		
	14.4	5.11		
	18.1	6.43		
MeOH only	22.6	2.77	−0.423	1.44
	28.3	3.76		
	39.9	5.30		

Table 4. Salt Effects ($LiClO_4$) on the Alkaline Hydrolysis of *S,S*-Diphenyl-*N*-bromosulfilimine (**1a (H,H)**) in 1/1 (v/v) MeOH/H_2O at 35.0 °C

[$LiClO_4$]	k_1×10⁴	k_2×10³	r
mol dm⁻³	s⁻¹	dm³ mol⁻¹ s⁻¹	
0	3.62	3.56	0.999
0.2	3.80	2.65	0.999
0.4	4.40	2.12	0.999
0.6	4.78	1.87	0.999

Table 3. The m Values for the Rate Constants on the Alkaline Hydrolysis of *S,S*-Diaryl-*N*-halosulfilimines, *o*-$YC_6H_4S(\rightarrow NX)C_6H_5$ (**1**) (35.0 °C)

X	Y	MeOH : H_2O	Y-value	k_1×10⁴	k_2×10³	m	m
		v : v		s⁻¹	dm³ mol⁻¹ s⁻¹	k_1	k_2
Br	H	2 : 1	1.19	1.35	2.74	0.638	0.153
		1 : 1	1.97	3.62	3.56		
		1 : 2	2.61	11.0	4.53		
Br	OMe	4 : 3	1.66	2.53	0.312	0.790	0.214
		1 : 1	1.97	4.30	0.270		
		3 : 4	2.26	7.16	0.396		
		1 : 2	2.61	14.3	0.460		
Cl	H	3 : 1	0.69	9.77	1.34	0.557	0.237
		2 : 1	1.19	17.3	1.49		
		5 : 3	1.39	22.7	2.22		
		4 : 3	1.66	31.6	2.19		
		1 : 1	1.97	51.0	2.59		

solvolysis of *t*-butylsulfonium ion, methyl chloride and methyl iodide gave the same rate in both solvents.[15] These examples are explained as the solvolysis of *t*-butyl chloride depends more on the electrophilic solvation in the rate-determining step and discriminates more difference in electrophilic nature of the solvent (H_2O is more electrophilic than D_2O) than the methyl halides.

The alkaline hydrolysis of **1a(H,H)** with excess NaOD was carried out in 1/1 (v/v) D_2O/MeOD, and was found to give k_H/k_D 1.25 for k_1 and 0.668 for k_2, respectively (Table 5). The effect for k_1 suggests that the solvolysis proceeds via S_N1-like mechanism promoted by the electrophilic solvation of the halide ion in the transition state. On the other hand, the isotope effect for k_2 suggests the S_N2-like mechanism which involves both the solvation and desolvation. However, the effect of the desolvation of oxygen may be larger than that of the solvation of bromide anion since the size of bromide anion is larger than oxygen of $^-$OH and $^-$OMe to weaken hydrogen bonding.

Ortho Substituent Effect. In order to examine the steric effect, the alkaline hydrolysis of *S*-(*o*-substituted phenyl)-*S*-phenyl-*N*-bromosulfilimines with excess NaOH was carried out in 1/1 (v/v) MeOH/H_2O. The rate constants obtained were listed in Table 1. Reduction of the reaction rates from those for the *p*-substituted derivatives were observed for both k_1 and k_2 of the methyl and methoxy substituents ($k_{1o\text{-}Me}/k_{1p\text{-}Me}$=0.317, $k_{2o\text{-}Me}/k_{2p\text{-}Me}$=0.116, $k_{1o\text{-}OMe}/k_{1p\text{-}OMe}$=0.214, $k_{2o\text{-}OMe}/k_{2p\text{-}OMe}$=0.0619, $k_{1p\text{-}OMe}$ and $k_{2p\text{-}OMe}$ were estimated from the Hammett plot). The ortho substituent effects for k_2 are larger than those for k_1 for both *o*-Me and *o*-OMe substituents suggesting that k_2 is more susceptible to the steric effect, if the electronic effects of ortho and para substituents are assumed to be the same. The solvent effect *m* values measured for the *o*-methoxy derivative (Table 3) are larger than those for **1a(H,H)** indicating an increase in S_N1-character due to the introduction of the ortho substituent group. However, the ratio $k_{1o\text{-}Me}/k_{1p\text{-}Me}$ (0.317) means that the reaction for k_1 is also subject to the steric effect, and the *m* value for k_1 for *S*-(*o*-methoxyphenyl)-*S*-phenyl-*N*-bromosulfilimine is considerably less than unity suggesting that the reaction for k_1 is not an ideal S_N1 solvolysis.

Table 5. Solvent Deuterium Kinetic Isotope Effect of the Alkaline Hydrolysis of *S,S*-Diphenyl-*N*-bromosulfilimine (**1a(H,H)**) with NaOD in 1/1 (v/v) D_2O/MeOD (35.0 °C)

[NaOD]×10²	k×10⁴	k_1×10⁴	k_2×10³
mol dm^{-3}	s^{-1}	s^{-1}	dm^3 mol^{-1} s^{-1}
5.31	5.71	2.90	5.33
10.6	8.66		
21.2	14.1		
42.5	25.6		

k_H/k_D=1.25 for k_1, k_H/k_D=0.668 for k_2.

Reactions of Other Halogen Derivatives. Rates for the solvolyses of *t*-butyl halides and neopentyl halides in 80% aqueous ethanol, which are considered to proceed via S_N1 mechanism, have been found to increase in such order as chloride<bromide<iodide (1.00 : 39.4 : 99[15] and 1.00 : 42.1 : 113[15] respectively). The formation of carbocation and halide ion is the rate-determining step for the solvolysis of *t*-butyl halides and neopentyl halides. Thus, the longer the bond length and the lower the bond energy (Cl<Br<I), the faster the reaction is. The same tendency has been observed for S_N2 reaction. For example, the reaction of propyl halides with sodium ethoxide in ethanol has been reported to increase in the same order (1.00 : 62.5 : 128).[16]

S,S-Diphenyl-*N*-chlorosulfilimine (**1b(H,H)**) and -*N*-iodosulfilimine (**1c[H,H]**) were also prepared and subjected to the alkaline hydrolysis. The rate constants and the *m* value for **1b(H,H)** obtained were listed in Tables 1 and 3. The product of the reaction of **1c(H,H)** was not the sulfoximine **2(H,H)** but *N*-unsubstituted *S,S*-diphenylsulfilimine. Therefore the rate of the hydrolysis is considered to be slower than that of the reduction. In this respect, the maximum limit of the hydrolysis rate of **1c(H,H)** was estimated from the rate of the reduction as shown in Table 1. The *m* values for **1b(H,H)** has a similar trend to those for **1a(H,H)**. The rate constants k_1 remarkably decreased in the following order N-chloro<N-bromo<N-iodo (1.00 : 0.071 : 0.044) as shown in Table 1, whose tendency is opposite to that in the reactions at carbon atom of alkyl halides. Unlike carbon atom, nitrogen has a lone pair of electrons to make the repulsion of the lone pairs of electrons between nitrogen and halogen in the reactants be important in determining the velocity of this reaction. Since the size of the orbital occupied with lone pair electrons of iodine is greater than chlorine, the polarizability of this orbital of iodine is greater than that of chlorine to reduce the repulsion. Therefore, the lone pair-lone pair repulsion of nitrogen and halogen may be greater in the order, N-I<N-Br<N-Cl. Furthermore, considering the character of the semipolar S-N bond of sulfilimine, partially negatively charged nitrogen increases the lone pair-lone pair repulsion to raise the energy level of reactants. On the other hand, the rate constants k_2 for **1a(H,H)** and **1b(H,H)** are close, which is probably the results of cancellation of the opposite tendencies of the leaving ability of halogen and the lone pair-lone pair repulsion.

General Base Catalysis. From the product analysis and the kinetic behavior, it is considered that the reaction for k_1 involves solvent nucleophiles H_2O and MeOH, while the reaction for k_2 involves both $^-$OH and $^-$OMe in the rate-determining step. The bond breaking of O-H is involved in the alkaline hydrolysis of **1a(H,H)** to afford **2(H,H)**. If the O-H bond break-

Table 6. Effects of the General Base Catalysis of the Alkaline Hydrolysis of *S,S*-Diphenyl-*N*-bromosulfilimine (**1a(H,H)**) in 1/1 (v/v) MeOH/H_2O

[Base]		$k\times10^4$	$k_1\times10^4$	$k_2\times10^3$
mol dm^{-3}		s^{-1}	s^{-1}	dm^3 mol^{-1} s^{-1}
NH_3[a]	0.08	4.33	4.29	0
	0.12	4.18		
	0.16	4.38		
	0.40	4.30		
$NaHCO_3$[b]	0.05	3.60	3.49	0.226
	0.10	3.71		
	0.15	3.82		
	0.20	3.94		

a) Temp 35.8±0.2 °C. b) Temp 34.9±0.6 °C.

ing by other bases is involved in the transition state, the acceleration of the reaction by general base catalysis can be expected. In order to examine possible assistance of general base to abstract the O-H proton in the rate-determining step, the alkaline hydrolysis of **1a(H,H)** in the presence of excess other base, e.g., NH_3 and $NaHCO_3$, was carried out in 1/1 (v/v) MeOH/H_2O. The rate constants obtained are listed in Table 6. In spite of the increase in the concentration of ammonia and $NaHCO_3$, the rate constants k_1 did not change, and k_2 was nearly zero, suggesting that the reaction does not involve general base catalysis, the O-H bond breaking in the rate-determining step.

Conclusion

Inspection of all the present results shows that a plausible reaction mechanism is as follows. The reaction rate can be divided into two parts, hydroxide anion independent and dependent. The former first-order reaction involves a rate-determining formation of a near nitridosulfonium cation containing a remaining weak N-X bond and a forming weak S-O bond with nucleophiles (H_2O, MeOH) as shown in Fig. 2. On the other hand, the latter second-order reaction occurs with S_N2-like mechanism involving a transition state in which the N-X bond cleavage is more progressed than the S-O bond formation.

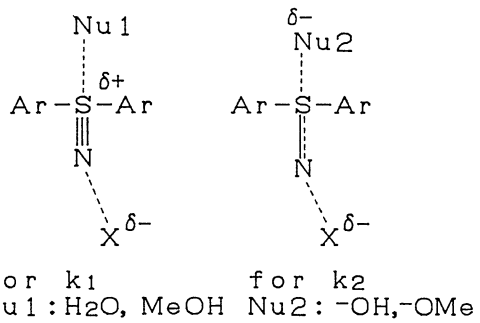


Fig. 2. The possible transition state structures of the reaction for k_1 and k_2.

Therefore, the transition states of the reactions for k_1 and k_2 are as follows.

The concurrent S_N1 and S_N2 reactions in such a present system is similar to the substitution reaction on the diphenylmethyl halides.[17,18]

This reaction is not only useful for the preparation of *S,S*-diarylsulfoximines (**2**) and *S,S*-diaryl-*S*-methoxythiazyne (**3**) but also the first interesting example to proceed via the solvolysis like mechanism on the tricoordinate sulfur atom.

Experimental

General. The IR spectra were taken on JEOL-810 and IRA-1 spectrometers. The ^1H NMR spectra were obtained on HITACHI R-24B spectrometer (60 MHz) in $CDCl_3$, CCl_4, and benzene using TMS as an internal standard. The UV spectra were measured on HITACHI EPS- 3T. In order to thermostat the UV cell was employed 10 mm thermostated cell holder, accessories of UV spectrometer. The MS spectra were obtained on JMS-D 300 spectrometer.

The reactions were monitored by TLC (MERCK, Kieselgel 60 GF), and the products were separated by column chromatography using Merck Kieselgel 60 silica gel.

All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co. Ltd. or Aldrich Chemical Co.. The reagents and solvents used were further purified by general methods.

***N*-Halosulfilimines.** *S,S*-Diaryl-*N*-halosulfilimines (**1**) were prepared according to the known method.[1,2] The physical properties of **1** prepared are as follows (Table 7, 8).

Table 7. IR Spectra of *S,S*-Diaryl-*N*-bromosulfilimines, $XC_6H_4S(\rightarrow NBr)C_6H_4Y$ (**1a**)

X	Y	ν_{SN}[a]	Mp
		cm^{-1}	°C
H	H	860[2]	96.0—97.0 (decomp)[2]
p-Me	*p*-Me	860	92.0—92.5 (decomp)
p-Me	H	860	89.5—90.0 (decomp)
p-Cl	H	870	85.0—85.5 (decomp)
m-Cl	H	865	103.5—104.5 (decomp)
o-Me	H	860 & 865	94.5—95.5 (decomp)
o-OMe	H	865	94.0—94.5 (decomp)

a) KBr method.

Table 8. Elemental Analysis of *S,S*-Diaryl-*N*-bromosulfilimines, $XC_6H_4S(\rightarrow NBr)C_6H_4Y$ (**1a**)

X	Y	Analytical data/%
p-Me	*p*-Me	Found C; 54.83, H; 4.63, N; 4.50
		Calcd C; 54.55, H; 4.58, N; 4.54
p-Me	H	Found C; 53.31, H; 4.09, N; 5.02
		Calcd C; 53.07, H; 4.11, N; 4.76
p-Cl	H	Found C; 45.50, H; 2.89, N; 4.95
		Calcd C; 45.81, H; 2.88, N; 4.45
m-Cl	H	Found C; 45.58, H; 2.81, N; 4.73
		Calcd C; 45.81, H; 2.88, N; 4.45
o-OMe	H	Found C; 50.22, H; 3.97, N; 4.88
		Calcd C; 50.33, H; 3.90, N; 4.52
o-Me	H	Found C; 52.97, H; 4.08, N; 4.98
		Calcd C; 53.07, H; 4.11, N; 4.76

Kinetics. An aqueous methanol solution (2.7 ml) of sodium hydroxide (4—17×10^{-2} mol dm^{-3}) was placed in the absorption cell thermostated at 35 °C (±0.20 °C) for 40 min. Then 0.3 ml of *S,S*-diaryl-*N*-halosulfilimines (**1**) (6—9±10 mol dm^{-3}) in methanol was pipetted into the solution and stirred rapidly to start the reaction. At regular time intervals, the absorbance of the solution was measured at the wavelength of 352 nm.

Rate constants were calculated by a least-squares method using the 8—30 points accumulated during the first 70% of reaction. When the data were plotted as $\ln(A_0-A_\infty/A_t-A_\infty)$ vs. time, where A_0 is the initial absorbance of **1**, A_t is the absorbance of **1** at a particular time and A_∞ is the absorbance of **1** at infinite time (more than 6 half-lives), a good linear correlation was observed, suggesting that the reaction rate follows a pseudo-first-order kinetics.

Activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$ were computer calculated by a least-squares method using $\ln k$ vs. $1/T$. The Hammett ρ value was computed by the least-squares method using σ values and logarithms of the rate constants.

Product Analysis. A prethermostated methanol solution of *S,S*-diphenyl-*N*-bromosulfilimine (**1a(H,H)**) (60 ml, 1.43×10^{-2} mol dm^{-3}) and an aqueous sodium hydroxide solution (30 ml, 7.23×10^{-2} mol dm^{-3}) were mixed into the glass-stoppered flask to start the reaction, and the flask was immersed in a thermostated bath (30—40 °C). After 1.5 hours, the solution was diluted with water until the total volume of the solution was about 150 ml. Then, the solution was treated by the next two methods to give the different products. The one is as follows. The solution was extracted with $CHCl_3$. The organic layer was washed with water, dried over anhydrous magnesium sulfate. After the solvent was evaporated, *S,S*-diphenylsulfoximine (**2,(H,H)**) was obtained in 34 % as a mixture with *S,S*-diphenyl-*S*-methoxythiazyne (**3(H,H)**) (60 %).[5] The other method involves once a treatment of the solution with aqueous HCl to acidify. Then the solution was alkalized again with NaOH, and extracted with $CHCl_3$. After the similar work-up, the sulfoximine **2(H,H)** was obtained in quantitative yield.

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