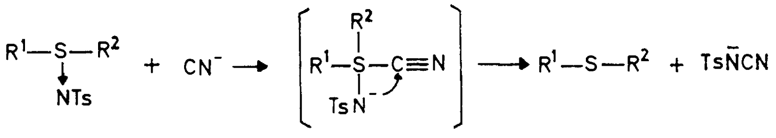
Reaction of *N-p*-Tolylsulphonylsulphimides with Halide Ion in Dimethylformamide

By **Shigeru Oae, Tetsuo Aida, and Naomichi Furukawa,*** Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka, Japan

The halide ion catalysed rearrangement of *N-p*-tolylsulphonylsulphimides $[\text{Ar}-\overset{+}{\text{S}}(\overset{-}{\text{N}}\text{Ts})-\text{R};\ \text{R} = \text{Me or PhCH}_2]$ was found to afford nearly quantitatively the corresponding sulphenamide [ArSN(Ts)R] and is considered to proceed through a Stevens-type intramolecular rearrangement. The kinetic study revealed that the rate of the reaction of *S*-aryl-*S*-methyl-*N-p*-tolylsulphonylsulphimides with lithium chloride in dimethylformamide obeys a second-order kinetic equation $v = k_2$ [Sulphimide][LiCl]. However, the lithium chloride concentration remained constant throughout the reaction, *i.e.* $v = k_{\text{app}}$ [Sulphimide]. This suggests that the reaction is catalysed by chloride ion. Furthermore, with only a 1/10 molar amount of lithium chloride the sulphimide afforded the rearranged product quantitatively. The activation parameters for the reaction are $\Delta H^{\ddagger}$ 26·7 kcal mol^{-1} and $\Delta S^{\ddagger}$ −4·1 cal mol^{-1} K^{-1} respectively, and a Hammett ρ value of +1·7 was obtained. When the reaction of *S*-methyl-*S*-phenyl-*N-p*-tolylsulphonylsulphimide with LiCl was carried out in the presence of benzyl chloride, the only rearranged product obtained was *N*-benzyltoluene-*p*-sulphonamide. Methyl chloride formed in this reaction was trapped as methyl *p*-tolyl sulphide upon addition of toluene-*p*-thiolate. These observations suggest that the catalytic rearrangement proceeds through initial formation of alkyl halide and subsequent alkylation of sulphenamide anion involving a rate-determining nucleophilic attack of halide ion on the α-carbon atom attached to the trivalent sulphur atom of the sulphimide.

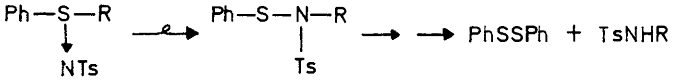
RECENTLY, Cram and his co-workers[1] showed that the alkaline hydrolysis of *S*-aryl-*S*-methyl-*N-p*-tolylsulphonylsulphimide to the corresponding sulphoxide proceeds through nucleophilic attack of hydroxide ion on the sulphur atom with inversion of configuration at the trivalent sulphur atom. Meanwhile, we found that the *N-p*-tolylsulphonylsulphimides react smoothly with nucleophiles such as cyanide ion[2] or triphenylphosphine[3] affording the corresponding sulphides. A kinetic study[4] suggested that the reactions proceed *via* initial formation of a tetraco-ordinate intermediate (Scheme 1).



Ts = p-MeC$_6$H$_4$SO$_2$

SCHEME 1

In a further extension of nucleophilic substitutions on the trivalent sulphur atom, several *N-p*-tolylsulphonylsulphimides were subjected to reaction with halide ion in dimethylformamide (DMF) or dimethyl sulphoxide (DMSO). The reaction proceeded smoothly to afford the rearranged product which eventually decomposed to the disulphide and *N*-alkyltoluene-*p*-sulphonamide in nearly quantitative yield. Although pyrolysis of *S*-alkyl-*S*-phenyl-*N-p*-tolylsulphonylsulphimides in dipolar aprotic solvents is also known to give the rearranged products,[5] this reaction usually requires more drastic reaction conditions, *e.g.*, heating a DMF solution at 180° in a sealed tube; the yields in this case are low.



R = Me or PhCH$_2$

The most notable feature of our reaction is that the rearrangement is apparently halide ion catalysed.

RESULTS AND DISCUSSION

Preparation of Sulphimides.—The *N-p*-tolylsulphonylsulphimides can readily be prepared by the modified Mann–Pope reaction[6] of the corresponding sulphides with sodium salt of chloramine T in the presence of a weak acid.

Reaction of Sulphimides with Halide Ion.—The reaction was carried out by heating the sulphimide and lithium halide in a dipolar aprotic solvent. The products and yields are shown in Table 1.

The products were identified as diaryl disulphide and *N*-alkyltoluene-*p*-sulphonamide by comparing m.p.s,

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[1] J. Day and D. J. Cram, *J. Amer. Chem. Soc.*, 1965, **87**, 4398; D. J. Cram, J. Day, D. D. Rayner, D. M. von Schriltz, D. J. Duchamp, and D. C. Garwood, *ibid.*, 1970, **92**, 7369; D. R. Rayner, D. M. von Schriltz, J. Day, and D. J. Cram, *ibid.*, 1968, **90**, 2721.

[2] S. Oae, T. Aida, K. Tsujihara, and N. Furukawa, *Tetrahedron Letters*, 1971, 1145.

[3] T. Aida, N. Furukawa, and S. Oae, *Chem. Letters*, 1973, 805; 1974, 121.

[4] S. Oae, T. Aida, and N. Furukawa, *Internat. J. Sulphur Chem.*, 1973, **8**, 73.

[5] N. Furukawa, T. Aida, and S. Oae, unpublished results.

[6] F. G. Mann and W. J. Pope, *J. Chem. Soc.*, 1922, **121**, 1052.

i.r. and n.m.r. spectra, and g.l.c. behaviour with those of authentic samples.

An interesting feature of the reaction is that a rearranged product, *N*-methyl-*N*-*p*-tolylsulphonylbenzenesulphenamide [PhSN(Ts)Me], was isolated from the reaction of *S*-methyl-*S*-phenyl-*N*-*p*-tolylsulphonsulphimide with lithium chloride in a good yield. The sulphenamide was isolated by quenching the reaction mixture in cold water and extracting with benzene and it was identified by m.p., elemental analysis, and i.r. and n.m.r. spectra.

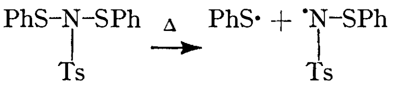
TABLE 1

Reaction of *N*-*p*-tolylsulphonylsulphimide $R^1\overset{+}{S}(\overset{-}{N}Ts)R^2$ with halide ion X [a]

R^1	R^2	X	Solvent	Temp. (°C)	t (h)	Yields (%) TsNHR [2]	R^1SSR^1	Others
Ph	Me	Cl	DMF	110	12	81	84	
Ph	Me	Br	DMF	110	12	72	59	
Ph	Me	I	DMF	110	12	64	52	I_2(13)
Ph	Me	Cl	DMSO	110	12	85	87	
Ph	Et [b]	I	DMF	110	12	60	86	CH_2=CH_2,$TsNH_2$ (21)
Ph	Pr^i [b]	I	DMF	110	12		67	CH_2=CHMe,$TsNH_2$ (30)
Ph	CH_2Ph	Cl	DMF	110	12	85	83	
Me	Me	I	DMF	110	12	6	12	$TsNH_2$ (22)
Ph	Me	Cl	DMF	110	1·5	12	10	$R^1SN(Ts)R^2$ (74)
o-$NO_2C_6H_4$	Me	Cl	DMF	110	0·5			$R^1SN(Ts)R^1$ (68)
Ph	Me [c]		DMF	110	12			*d*
Ph	Me [c]		DMF	180	3	50	40	*e*

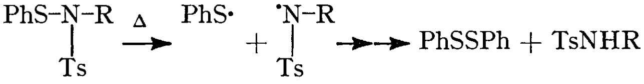
[a] Reactions were carried out with sulphimide (3 mmol) and lithium halide (12 mmol) in solvent (5 ml). [b] Sulphimides with at least one β-hydrogen atom undergo an E_i reaction. [c] The reactions were carried out in the absence of halide ion. [d] Starting material recovered quantitatively. [e] 22% Starting material recovered.

We found recently that the S–N linkage of *NN*-bisphenylthiotoluene-*p*-sulphonamide readily undergoes the homolytic cleavage (1) upon pyrolysis to give radicals.[7] Thus, the formation of disulphide and amide



$$\mathrm{PhS{-}\underset{Ts}{\underset{|}{N}}{-}SPh} \xrightarrow{\Delta} \mathrm{PhS^{\bullet}} + \mathrm{{}^{\bullet}\underset{Ts}{\underset{|}{N}}{-}SPh} \qquad (1)$$

in the present reaction may also be attributed to the initial free radical cleavage (2).



$$\mathrm{PhS{-}\underset{Ts}{\underset{|}{N}}{-}R} \xrightarrow{\Delta} \mathrm{PhS^{\bullet}} + \mathrm{{}^{\bullet}\underset{Ts}{\underset{|}{N}}{-}R} \longrightarrow\!\!\rightarrow \mathrm{PhSSPh} + \mathrm{TsNHR} \qquad (2)$$

All these observations suggest that the initial step of the reaction is migration of an alkyl group from the trivalent sulphur atom to nitrogen, the amide and disulphide being formed by subsequent pyrolysis. The yield of the rearranged product greatly depends on the structure of the sulphimide; for instance, *S*-alkyl-*S*-aryl-*N*-*p*-tolylsulphonylsulphimides which have no β-hydrogen atoms always give the corresponding rearranged products.

Kinetics and Hammett Correlation.—In order to clarify the mechanism, the kinetics were examined by following the increase in the concentration of *N*-alkyltoluene-*p*-sulphonamide. In the presence of a 1/10 molar quantity of LiCl *S*-methyl-*S*-phenyl-*N*-*p*-tolylsulphonylsulphimide was completely consumed. This suggests that the reaction is catalysed by chloride ion. Accordingly, the rate of rearrangement (3) should obey the kinetic equation (4) if $k \gg k_1$.* The apparent first order rate constants are

$$\text{Sulphimide} + \mathrm{Cl^-} \underset{k_1}{\overset{k_2}{\rightleftharpoons}} [\text{Sulphimide–Cl}] \xrightarrow{k_3} \text{Product} + \mathrm{Cl^-} \qquad (3)$$

$$\text{Rate} = k_2\,[\text{Sulphimide}][\text{LiCl}] = k_{app}\,[\text{Sulphimide}] \qquad (4)$$

shown in Table 2. Although the rate of reaction satisfies equation (4) at a given LiCl concentration, it is

TABLE 2

Rate constants of the reaction of *S*-methyl-*S*-phenyl-*N*-*p*-tolylsulphonylsulphimide with LiCl in DMF at 118·00 ± 0·02 °C

[Sulphimide] = 0·0625M, [LiCl] = 0·125M

Completion (%)	$10^5k_{app}/s^{-1}$	$10^4k_2/l\ mol^{-1}\ s^{-1}$
5·31	(14·93)	(11·94)
12·02	15·22	12·18
20·68	16·07	12·86
25·03	16·88	13·50
37·19	16·33	12·73
58·90	15·84	12·17
70·29	15·91	12·73
Av.	16·04 ± 0·50	12·70 ± 0·45

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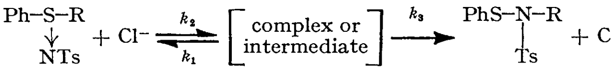
* Product analyses and kinetic results lead to the reaction scheme (i). Based on this the kinetic equations (ii)—(iv) are



$$\mathrm{Ph{-}\underset{NTs}{\underset{\downarrow}{S}}{-}R} + \mathrm{Cl^-} \underset{k_1}{\overset{k_2}{\rightleftharpoons}} \left[\begin{array}{c}\text{complex or}\\ \text{intermediate}\end{array}\right] \xrightarrow{k_3} \mathrm{PhS{-}\underset{Ts}{\underset{|}{N}}{-}R} + \mathrm{Cl^-} \qquad \text{(i)}$$

obtained by the steady state method. The choice between

$$\text{Rate} = k_2/(1 - k_1/k_3)[\mathrm{Cl^-}][\text{Sulphimide}] \qquad \text{(ii)}$$

$$\text{if } k_3 \ll k_1 \text{ Rate} = K\,k_3\,[\mathrm{Cl^-}][\text{Sulphimide}] \quad (K = k_2/k_1) \qquad \text{(iii)}$$

$$\text{if } k_3 \gg k_1 \text{ Rate} = k_2\,[\mathrm{Cl^-}][\text{Sulphimide}] \qquad \text{(iv)}$$

equations (iii) and (iv) is governed by the effect of substituents on *S*-methyl-*S*-phenyl-*N*-(*para*-substituted phenylsulphonyl)sulphimide, *i.e.*, $k_3 \gg k_1$ requires that electron-releasing substituents accelerate the reaction. The results show that the *p*-Br derivative reacts faster than the *p*-Me one. This indicates that the reaction involves rate-determining nucleophilic attack ($k_3 \gg k_1$) by halide ion.

[7] S. Oae and T. Tsuchida, *Bull. Chem. Soc. Japan*, 1972, **45**, 2856.

also enhanced remarkably by an increase in the LiCl concentration, while in the absence of LiCl the reaction does not occur. Thus the rate depends upon the concentration of LiCl. The kinetic results obtained by changing the LiCl concentration are summarized in Table 3. By plotting log [LiCl] against log k_{app} a straight line (slope 1·1) was obtained (Figure 1). Thus, the reaction is first order in both sulphimide and LiCl.

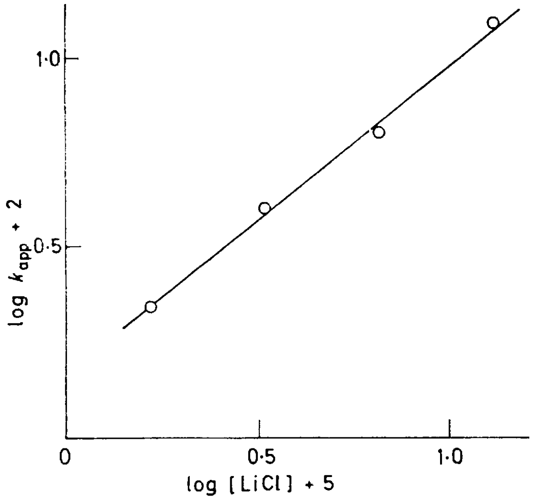


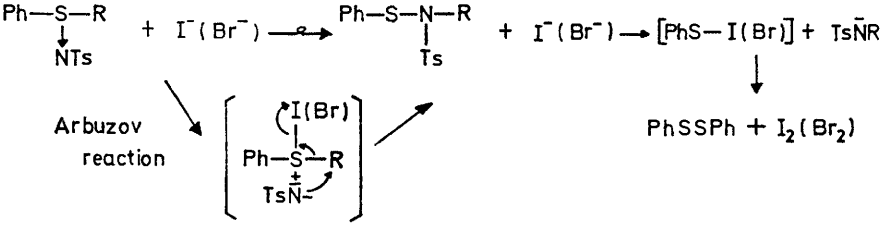
FIGURE 1 Correlation of log k_{app} and log[LiCl] at 109·3 °C

The activation parameters for the reaction of *S*-methyl-*S*-phenyl-*N*-*p*-tolylsulphonylsulphimide with LiCl in DMF are $\Delta H^‡$ 26·7 ± 0·4 kcal mol^{-1} and $\Delta S^‡$ −4·1 ± 1·1 cal mol^{-1} K^{-1}. The second-order rate constants of the reactions between the *para*-substituted *S*-methyl-*S*-phenyl-*N*-*p*-tolylsulphonylsulphimide and LiCl give a good Hammett correlation[8] with ρ +1·7 (Table 4).

TABLE 3

Correlation of k_{app} and [LiCl] at 115·00 ± 0·02 °C

[LiCl]/M	0·0167	0·0333	0·0667	0·1333
10^5k_{app}/s^{-1}	2·19 ± 0·08	4·08 ± 0·12	6·18 ± 0·17	12·43 ± 0·36



SCHEME 2

Effect of Halide Ion.—The effect of halide ion was investigated for the reaction of *S*-methyl-*S*-phenyl-*N*-*p*-tolylsulphonylsulphimide with lithium chloride, bromide, and iodide. The calculated k_{app} values for these reactions were plotted against time (Figure 2) and the rate constants for the bromide and iodide show considerable deviation from the values calculated by equation (4), and only for the chloride do they remain constant throughout the reaction. For bromide or iodide the kinetic equation does not hold and their concentration decreases or is consumed by side reactions such as shown in Scheme 2.

TABLE 4

Rate constants of the reaction of p-$XC_6H_4\overset{+}{S}(\overset{-}{N}Ts)Me$ with LiCl in DMF

[Sulphimide] = 0·0625M, [LiCl] = 0·125M

X	Temp. (°C)	10^4k_2/ l mol^{-1} s^{-1} [a]	
H	100·00 ± 0·02	2·32 ± 0·06	$\Delta H^‡$ = 26·7 ± 0·4 kcal/
H	110·00 ± 0·02	6·00 ± 0·12	mol^{-1}
H	118·00 ± 0·02	12·75 ± 0·34	$\Delta S^‡$ = −4·1 ± 1·1 cal
Cl	118·00 ± 0·02	29·31 ± 0·65	mol^{-1} K^{-1}
CH_3	118·00 ± 0·02	6·67 ± 0·22	ρ_X = +1·7 (r 0·999)
CH_3O	118·00 ± 0·02	4·13 ± 0·14	

[a] Average of at least two runs.

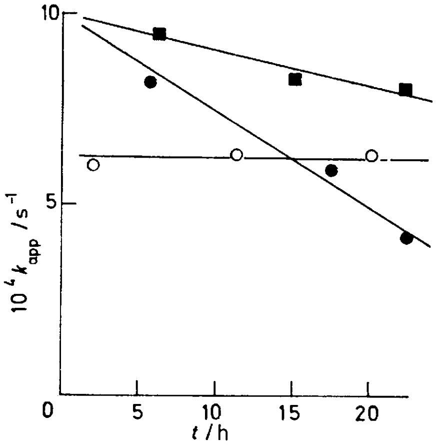


FIGURE 2 Effect of halide ion on k_{app}: ○, Cl⁻; ■, Br⁻; ●, I⁻

In the case of LiBr or LiI, I_2 or Br_2[9] was liberated during the reaction. However, even for these halides, the initial rate constants of the reaction can be estimated from Figure 2, and the relative reactivities of the halide ions is in the order Br⁻ ≳ I⁻ > Cl⁻. However, an important question still remains, namely, to what extent do lithium salts LiX dissociate to give free halide ions in a dipolar aprotic solvent as such as DMF? Although LiCl is incompletely dissociated, KBr and KI are completely ionized in DMF.[10] This work[10] showed

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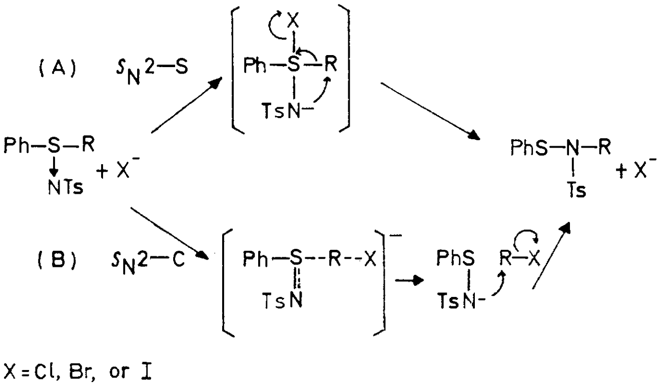
[8] L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1940, p. 188.

[9] T. Aida, N. Furukawa, and S. Oae, *Tetrahedron Letters*, 1973, 3853.

[10] J. E. Prue and P. J. Sherrington, *Trans. Faraday Soc.*, 1961, **57**, 1795; D. P. Ames and P. G. Sears, *J. Phys. Chem.*, 1955, **59**, 16.

that 5.6×10^{-3}M-LiCl in DMF is 90% dissociated. Since the concentration of LiCl in this study is substantially higher the degree of dissociation should be lower. Assuming 80% dissociation the initial rate constants are similar, *i.e.*, $Br^- \gtrsim I^- \approx Cl^-$. The order of nucleophilicity of halide ions, $I^- > Br^- > Cl^-$, in protic solvents is often regarded as strong evidence for polarizability as a determining factor; however, in dipolar aprotic solvents such as DMF in which the anion is unsolvated the order of nucleophilicity is $Cl^- \approx Br^- > I^-$.[11]

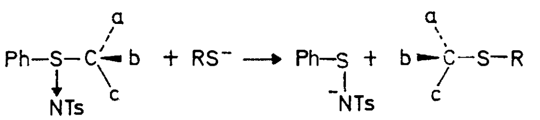
On the basis of the product and kinetic analysis, together with previous results for the reactions of sulphimides with nucleophiles such as CN^-, PhS^-, or Ph_3P, two mechanisms are conceivable (Scheme 3). One is initial rate-determining attack by halide ion on the trivalent sulphur atom, affording an intermediate which collapses to the final products (S_N2–S). The other is rate-determining attack by halide ion on the α-carbon atom attached to the trivalent sulphur atom giving the *N*-*p*-tolylsulphonylsulphenamide anion and alkyl halide which rapidly recombine to give the rearranged products (S_N2–C).



SCHEME 3

The rate-determining step is obviously either initial *S*- or *C*-attack, since toluene-*p*-sulphonamide anion and *N*-phenylthiotoluene-*p*-sulphonamide anion reacts smoothly with alkyl halides even at room temperature in DMF. Furthermore, when *S*-methyl-*S*-phenyl-*N*-*p*-tolylsulphonylsulphimide was treated with LiCl in the presence of benzyl chloride, *N*-benzyltoluene-*p*-sulphonamide was isolated as the sole rearranged product, and methyl chloride was also detected by trapping it as methyl *p*-tolyl sulphide by the addition of toluene-*p*-thiolate, thus indicating that the mechanism shown in Scheme 3(A) can be ruled out.

We have shown recently that the reaction of *N*-*p*-tolylsulphonylsulphimide with thiolate ion is a typical S_N2 process with attack on the α-carbon atom attached to the trivalent sulphur atom [reaction (5)].[12] This observation suggests that the catalytic rearrangement described here proceeds through initial formation of



$$\underset{\downarrow\atop NTs}{Ph{-}S}{-}C\overset{a}{\underset{c}{\leftarrow}}b + RS^- \longrightarrow \underset{-|\atop NTs}{Ph{-}S} + b{\rightarrow}\overset{a}{\underset{c}{C}}{-}S{-}R \quad (5)$$

alkyl-halide and subsequent alkylation of the sulphenamide anion involving rate-determining nucleophilic attack of halide ion on the α-carbon atom attached to the trivalent sulphur atom [Scheme 3(B)].

EXPERIMENTAL

Materials.—*Sulphimides.* All the sulphimides used were prepared by treatment[13] of the corresponding sulphides with chloramine T in methanol. M.p.s and i.r. and n.m.r. spectra agree with those of authentic samples.

Alkali-metal halides. Sodium, potassium, and lithium halides were commercial products which were used without further purification other than drying at 100 °C overnight *in vacuo*.

Solvents. All solvents were purified by the usual methods. DMF was dried over CaH_2 and redistilled before use.

Preparation of N-*Alkyltoluene*-p-*sulphonamides.*—Typically, an aqueous solution of alkylamine (20 mmol) was added to an acetone solution of toluene-*p*-sulphonyl chloride (10 mmol) at room temperature. After 1 h the mixture was poured into water and the crystalline precipitate was filtered and recrystallized from ethanol. Yields were *ca.* 95%.

Reaction of N-p-*Tolylsulphonylsulphimides with Halide Ion.*—Typically, a mixture of *S*-methyl-*S*-phenyl-*N*-*p*-tolylsulphonylsulphimide (3 mmol) and lithium chloride (12 mmol) was dissolved in DMF (5 ml). The solution was heated in a sealed tube at 110 °C for 12 h. The contents were then poured into cold water (30 ml), the solution was extracted, and the products were separated by column chromatography (silica gel; benzene). The products obtained were *N*-methyltoluene-*p*-sulphonamide (2·4 mmol, 81%), identical with an authentic sample, and diphenyl disulphide (2·5 mmol, 84%).

Preparation of N-*Methyl*-N-p-*tolylsulphonylbenzenesulphenamide.*—A mixture of *S*-methyl-*S*-phenyl-*N*-*p*-tolylsulphonylsulphimide (3 mmol) and lithium chloride (12 mmol) was dissolved in DMF (5 ml) in a sealed tube heated at 110 °C for 1·5 h. The contents were then poured into cold water (50 ml), and a crystalline *precipitate* (83%) which separated was washed with n-hexane and recrystallized from n-hexane–benzene (74%), m.p. 89—90 °C (Found: C, 57·0; H, 4·95; N, 4·7. $C_{14}H_{15}NO_2S_2$ requires C, 57·4; H, 5·1; N, 4·8%).

Reaction of S-*Methyl*-S-*phenyl*-N-p-*tolylsulphonylsulphimide with Lithium Chloride in the Presence of Benzyl Chloride.*—A mixture of the sulphimide (3 mmol), lithium chloride (12 mmol), and benzyl chloride (3 mmol) was dissolved in DMF (5 ml) in a sealed tube and heated at 110 °C for 12 h. The tube was cooled in dry ice–methanol and broken and a solution of sodium toluene-*p*-thiolate (3 mmol) in DMF was added. The tube was resealed and left overnight at room temperature. The contents were poured into cold water (30 ml) and the products were extracted and separated

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[11] A. J. Parker, *J. Chem. Soc.*, 1961, 1328; S. Winstein, L. G. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Letters*, 1960, 24.

[12] S. Oae, T. Aida, M. Nakajima, and N. Furukawa, unpublished results.

[13] K. Tsujihara, N. Furukawa, K. Oae, and S. Oae, *Bull. Chem. Soc. Japan*, 1969, **42**, 2631.

by column chromatography (silica gel; benzene). The yield of methyl *p*-tolyl sulphide was determined by g.l.c. The products obtained were *N*-benzyl toluene-*p*-sulphonamide (2·6 mmol, 86%), diphenyl disulphide (2·0 mmol, 67%), and methyl *p*-tolyl sulphide (2·2 mmol, 73%).

Kinetic Procedures.—A typical procedure was as follows. DMF solutions of 0·125M-lithium chloride and 0·0625M-*S*-methyl-*S*-phenyl-*N*-*p*-tolylsulphonylsulphimide were placed separately into a thermostatted bath. The two solutions were then mixed and aliquot portions (1·0 ml) were removed at intervals with a pipette. The solutions were quenched immediately with aqueous 0·1N-NaOH solution (4 ml), left for 0·5 h, and then benzene (2 ml) was added. The benzene layer was removed, the mother solution was acidified by concentrated HCl, and a chloroform solution (2 ml) of *NN*-dimethyltoluene-*p*-sulphonamide (0·02M; g.l.c. standard) was added. G.l.c. conditions were: 1 m × 3 mm column of PEG-20M on Celite; stainless steel tube; 245 °C; H_2 flow, 65 ml min^{-1}. Rate constants were calculated from equation (4). Activation parameters and the Hammett correlation were calculated as usual.

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