BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1622—1627 (1969)

The Alkaline Ethanolyses of Chlorophenyldiphenylsulfonium Halides, Chlorophenyl Phenyl Sulfones and Chloronitrobenzene in Aqueous Ethanol[1]

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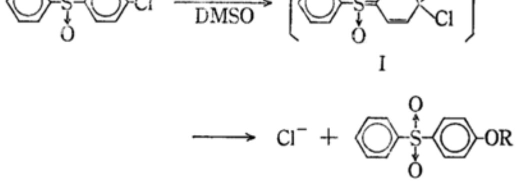
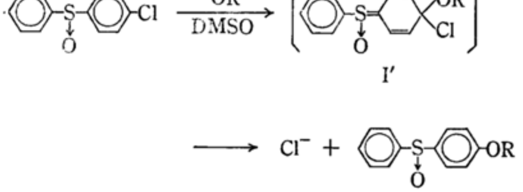
(Received September 5, 1968)

o-, *m*-, and *p*-Chlorophenyldiphenylsulfonium halides were prepared and subjected to the alkaline ethanolysis in order to compare the activating effects of *o*-, *m*-, and *p*-diphenylsulfonio groups with those of *o*-, *m*-, and *p*-phenylsulfonyl and nitro-groups. The diarylsulfonio group at either ortho or para position was found to facilitate the nucleophilic substitution of aryl chloride powerfully. While the effect of diarylsulfonio group was not only substantially larger than that of phenylsulfonyl group, but also exceeding even that of nitro group. Meanwhile, with ethoxide ion in ethanol the alkaline decomposition reaction, presumed to be initiated by the attack of ethoxide on the sulfur atom of chlorophenyldiphenylsulfonium halide, occurred competitively along with the S_N reaction, but the rate of the S_N reaction of *p*-chlorophenyldiphenylsulfonium perchlorate was found to be about 9 times larger than that of the decomposition reaction. Substitution of a methyl group at ortho to diphenylsulfonio, phenylsulfonyl and -sulfinyl groups did change very little the rates of the ethanolyses of the corresponding *p*-substituted chlorobenzenes, suggesting that essentially there is no or little steric inhibition for the 3d-orbital resonance with either sulfonio, sulfinyl, or sulfonyl group in the S_N reaction of these compounds.

In the previous paper,[1] dealing with the alkaline hydrolyses of chlorophenyl phenyl sulfones and sulfoxides in aqueous dimethyl sulfoxide, we have shown that both phenylsulfonyl and -sulfinyl groups at either *o*- or *p*-positions markedly accelerate the aromatic S_N reaction of hydrolysis.

This reaction is presumed to involve the initial formation of an addition intermediate (I or I′) which is undoubtedly stabilized by the 3d-orbital conjugative effect of phenylsulfonyl or phenylsulfinyl group.





In the nucleophilic substitution of aromatic halides, an electron-accepting group such as sulfonyl or nitro group, is known to accelerate the rate especially when the group is located at either ortho or para to the halogen group.[2] Meanwhile the acidity constants[3] of *m*- and *p*-methylsulfinyl, sulfonyl and dimethylsulfonio-phenols reveal that the sulfonio group at *p*-position can display a relatively strong electron-accepting 3d-orbital resonance effect, and its effect is even larger than that of the corresponding sulfonyl group. Therefore, the sulfonio group when substituted at either ortho or para-position is expected to facilitate the alkaline hydrolysis substantially more than when substituted at meta-position, while the ethanolysis of the sulfonio-substituted chlorobenzene will be much faster than the corresponding sulfonyl compound. In fact, *p*-dimethylsulfonic group is known to increase the reactivity of 2-nitrochlorobenzene more than *p*-trimethylammonio

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1) For previous work see: S. Oae and Y. H. Khim, This Bulletin, **40**, 1716 (1967).

2) H. R. Todd and R. L. Shriner, *J. Am. Chem. Soc.*, **56**, 1382 (1934).

3) a) S. Oae and C. C. Price, *ibid.*, **80**, 3482 (1958). b) C. C. Price and S. Oae, "Sulfur Bonding," Donald Press, New York, N. Y. (1962), Chapter 3. c) F. G. Bordwell and P. S. Bountan, *J. Am. Chem. Soc.*, **78**, 87 (1956).

group in the alkaline methanolysis.[4] However there is no quantitative data to compare the activating effects of sulfonio group with other corresponding sulfur groups. In order to examine the effect of sulfonio group in the aromatic S_N reaction we have synthesized comparatively more stable sulfonium salts, *i. e.*, *o*-, *m*- and *p*-chlorophenyldiphenylsulfonium perchlorate from diphenylethoxysulfonium tetrafluoroborate and chlorophenyl Grignard reagents and subjected to the alkaline S_N reactions in aqueous ethanol in order to compare the relative activating effect of diphenylsulfonio group with those of phenylsulfonyl and nitro groups.

Meanwhile, in view of the formation of the various products in the treatment of triarylsulfonium salt with bases, the alkaline decomposition is expected to give different products dependent on the nature of the bases. In fact, we have found that the reaction of triphenylsulfonium bromide with dimsyl anion in dimethyl sulfoxide gives diphenyl sulfide, benzene, thioanisole and *o*-methylmercaptophenol, while the treatment with piperidide anion gives diphenyl sulfide and phenylpiperidine; meanwhile the reaction with *p*-methylthiophenoxide ion also gave diphenyl sulfide and phenyl tolyl sulfide. In the case with ethoxide anion, diphenyl sulfide, benzene and aldol resins were obtained as main products together with a small amount of phenetole. The detailed mechanisms of these alkaline decompositions of triarylsulfonium halides will be reported in another paper.[5]

For the kinetic experiments of S_N and alkaline decomposition reactions, the ethoxide anion in aqueous ethanol was selected as the base. In this case the attack could occur at both the carbon atom bearing chlorine atom and the sulfur atom of the sulfonium salt. However, when *o*- and *p*-chlorophenyldiphenylsulfonium perchlorate were treated with potassium hydroxide in 70% (vol%) aqueous ethanol, both *o*- and *p*-ethoxyphenyldiphenylsulfonium perchlorate were the major isolable products, indicating that the reaction appears to proceed through a typical aromatic S_N path like in the cases of the sulfones and the sulfoxides[1] as reported in our previous paper.

The products obtained after the treatment with ethoxide in aqueous ethanol were carefully recrystallized and subjected to the IR, NMR, UV and elemental analyses. Since both hydroxide and ethoxide ion can exist in an equilibrium, one would expect to obtain both *p*-ethoxyphenyl- and *p*-hydroxyphenyl-diphenylsulfonium compounds, however, the *p*-hydroxyphenyl compound could not be detected among the products. This means that ethoxide ion being more nucleophilic than hydroxide ion, attacks preferentially the aromatic carbon undergoing the S_N reaction. While the alkaline decomposition reaction was expected to take place competitively with the aromatic S_N reaction, only under a prolonged heating diphenyl sulfide and benzene were obtained as the main products from the reaction of triphenylsulfonium bromide with ethoxide ion. Undoubtedly, this decomposition is initiated by the attack of ethoxide ion on the sulfur atom of the sulfonium salt.

Recently, Bunnett and Happer[6] demonstrated that *o*-chlorophenyl-triphenylphosphonium iodide reacts with sodium methoxide in methanol to afford triphenylphosphin oxide and chlorobenzene suggesting the reaction to proceed through a nucleophilic attack of methoxide ion on the phosphorus atom with the elimination of chlorobenzene.

The mode of the alkaline decomposition (or the nucleophilic attack on the sulfur atom) of triphenylsulfonium and *p*-chloro- or *p*-ethoxyphenyldiphenylsulfonium halides would be identical, and the ease of their alkaline decompositions would not be much different each other, since the effect of only one chloro group from para-position would be very small. Therefore, the rates of the aromatic S_N reaction of chlorophenyldiphenylsulfonium halides by ethoxide ion can be estimated by measuring the amounts of both the aromatic S_N reaction and the alkaline decomposition and correcting the amount of the alkaline decomposition into the aromatic S_N reaction of chlorophenyldiphenylsulfonium halides. Thus we have compared the relative magnitudes of the activating effect of diphenylsulfonio group with those of phenylsulfonyl, -sulfinyl and nitro groups in the aromatic S_N reaction of alkaline ethanolysis.

Results and Discussion

The alkaline decomposition of triarylsulfonium bromide was found to obey the second order kinetic rate law; first order with respect to both the sulfonium concentration and potassium hydroxide concentration as shown in Figs. 1 and 2. The results of the alkaline decompositions of triarylsulfonium halides are shown in Table 1.

The rates of the aromatic S_N ethanolyses of *o*- and *p*-chlorophenyldiphenylsulfonium perchlorate which are corrected with that of the alkaline decomposition of triphenylsulfonium perchlorate are shown in Table 2 along with those of similar aromatic S_N reactions of chloronitrobenzenes and chlorophenyl phenyl sulfones. The rates of the sulfones at 105°C are calculated by extrapolating the values at 155°C using their activation

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[4] N. J. Daly, G. Durger and J. Miller, *Aust. J. Chem.*, **11**, 290 (1958).

[5] The details of this study will be reported later.

[6] J. F. Bunnett and D. A. R. Happer, *J. Org. Chem.*, **32**, 2701 (1967).

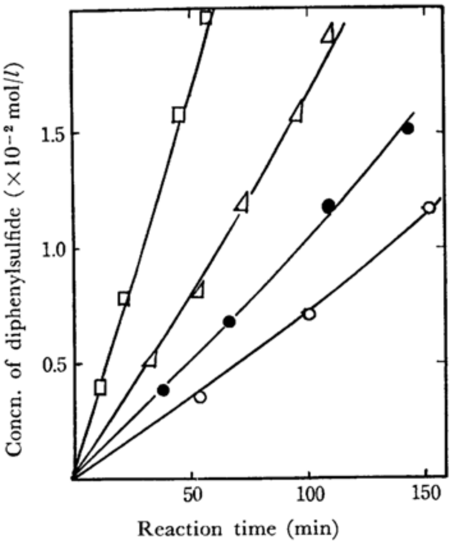


Fig. 1. The dependence of the mole of diphenyl sulfide on the sulfonium salt concentration.
[KOH]: 2.69×10^{-1} mol/l: constant
□, Salt/KOH=1/2 Δ, Salt/KOH=3/8
●, Salt/KOH=1/4 ○, Salt/KOH=1/8

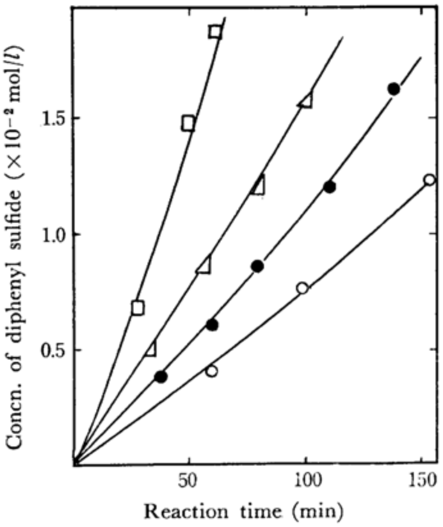


Fig. 2. The dependence of the mole of diphenyl sulfide on the potassium hydroxide concentration.
[Salt]: 7.806×10^{-2} mol/l: constant
□, KOH/Salt=8 Δ, KOH/Salt=4
●, KOH/Salt=3 ○, KOH/Salt=2

parameters.

All the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are also shown in Table 2. When the relative rates of the sulfonium perchlorates are compared with those of the sulfones and the nitrobenzenes, one finds that the activating effects of diphenylsulfonio group are markedly larger than those of the corresponding phenylsulfonyl and even exceed those of nitro groups.

Unfortunately, the rate of the aromatic S_N reaction of the *m*-isomer of the sulfonium perchlorate cannot be obtained directly because the aromatic S_N reaction is apparently so slow that the alkaline decomposition takes place faster than the S_N reaction, leading to the preferential decomposition. This means, however, that the S_N reaction of both the *o*- and *p*-sulfonium perchlorates are markedly faster than that of the *m*-isomer, since the S_N reaction of the *p*-isomer is nearly ten times faster than the decomposition of triphenylsulfonium perchlorate.

Our previous assumption that the reactivity of the alkaline decomposition of chlorophenyldiphenylsulfonium perchlorate is nearly the same as that of triphenylsulfonium perchlorate, would be quite valid because there is little or negligible difference in the rates of the decomposition of triphenyl- and tritolyl-sulfonium bromides. Thus, the markedly increased reactivities of the ortho- and para-isomers over that of the *m*-isomer is undoubtedly associated with the 3d-orbital conjugative effect of the diphenylsulfonio groups to stabilize the intermediate complex (III and IV) rather than their

TABLE 1. ALKALINE DECOMPOSITION OF TRIARYLSULFONIUM BROMIDE WITH POTASSIUM HYDROXIDE IN 70% AQUEOUS ETHANOL AT 105±0.1°C

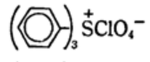
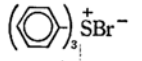
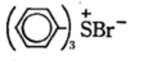
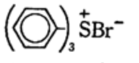
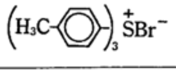
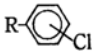
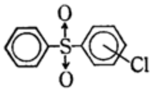
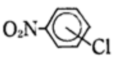
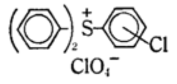
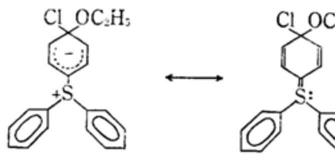
Compound	Sulfonium halide (concentration) mol l^{-1}	KOH mol l^{-1}	k_2 l mol^{-1} sec^{-1}
	7.93×10^{-2}	27.6×10^{-2}	1.21×10^{-4}
	7.78×10^{-2}	22.0×10^{-2}	1.42×10^{-4}
	7.81×10^{-2}	26.7×10^{-2}	1.53×10^{-4}
	5.96×10^{-2}	22.47×10^{-2}	1.62×10^{-4}
	$7.6\ \times10^{-2}$	15.8×10^{-2}	1.33×10^{-4}

TABLE 2. THE S_N2 REACTIONS OF CHLOROPHENYLSULFONIUM PERCHLORATES, CHLOROPHENYL SULFONES AND CHLORONITROBENZENES WITH ETHOXIDE ION IN AQUEOUS ETHANOL* AT 105 ± 0.1°C

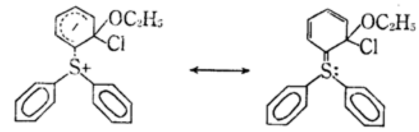
Compounds 		k_2 $l\,\mathrm{mol}^{-1}\,\mathrm{sec}^{-1}$	rel. rate (total)	rel. rate (with in the isomers)	$\Delta H^{\neq}$ kcal	$\Delta S^{\neq}$ (eq)
	*m*-Cl	1.40×10^{-7}	1	1	22	−38
	p-Cl	3.30×10^{-6}	24	24	20	−26
	o-Cl	1.41×10^{-6}	10	10	20	−34.9
	*m*-Cl	5.80×10^{-6}	41	1		
	p-Cl	3.63×10^{-4}	2600	65	21	−20
	o-Cl	1.52×10^{-4}	1010	45	19	−24
	*m*-Cl	**	—	—	—	—
	p-Cl	1.15×10^{-3}	8215	1.54	22.9	−11.4
	o-Cl	7.50×10^{-4}	5300	1.0	21.2	−17.1

* The volume ratio of ethanol and water in the reaction is 7 : 3.

** The decomposition of sulfonium halide is much faster than the S_N2 reaction of *m*-isomer.



(III)



(IV)

inductive effect, like in the similar cases of the sulfoxide and the sulfones reported previously.[1]

In the previous cases of the aromatic S_N reactions of chlorophenyl phenyl sulfones and chloronitrobenzenes, the *p*-isomers are the most reactive in both cases and the relative rate of the *p*-sulfone is 24 times as that of the *m*-isomer.

Earlier, the theoretical considerations[7] and the studies of dissociation constants[8] of various sulfoxides, sulfones and sulfonium halides have revealed that the 3d-orbital resonance effect is quite stereo-insensitive. In seeking further supporting evidence for the stereo-insensitivity of the 3d-orbital resonance, we have synthesized sterically crowded sulfoxide, sulfone and sulfonium perchlorate which have one methyl group at ortho position and subjected them to the kinetic experiments of the alkaline ethanolysis in aqueous ethanol for both the sulfone and the sulfonium compound and the hydrolysis in aqueous dimethyl sulfoxide for the sulfoxide. The kinetic results are shown in Table 3.

Inspection of the data reveals clearly that the electron-accepting conjugative effects of diphenylsulfonio, phenylsulfonyl and sulfinyl groups are not much inhibited by the bulky ortho methyl group at the *o*-position. The small reductions of the rates by the substitution of *o*-methyl group are undoubtedly due to the electron-releasing inductive effect of methyl group.

This may serve another evidence to support that there is little or almost no steric hindrance in the electron-accepting type conjugation involving 3d-orbital resonance of the sulfur atom.

Experimental

_o_-, _m_- and _p_-Chlorophenyldiphenylsulfonium Perchlorate. The titled compounds were prepared by the method of Andersen.[9] Diphenyl sulfoxide (8 g) was dissolved in 15 m*l* of anhydrous methylene chloride containing triethyloxonium tetrafluoroborate[10] (8.6 g). After the solution was stirred for about 30 min at room temperature, 50 m*l* of anhydrous ethyl ether was added to this solution and then the methylene chloride - ethyl ether mixture was replaced by tetrahydrofuran by decantation. This solution of ethoxydiphenylsulfonium tetrafluoroborate[11] was slowly added to the Grignard reagent prepared from *p*-chlorobromobenzene (20.4 g) and magnesium (2.7 g) in anhydrous

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[7] a) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940). b) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

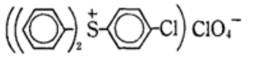
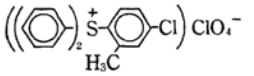
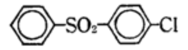
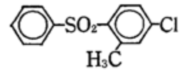
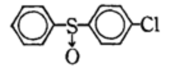
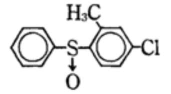
[8] a) H. Kloosterziel and H. von J. Basper, *Rec. Trav. Chim.*, **72**, 185 (1953). b) W. E. Doering and L. K. Levy, *J. Am. Chem. Soc.*, **77**, 509 (1955). c) E. A. Fehnel and M. Carmack, *ibid.*, **79**, 1291 (1950).

[9] K. K. Andersen and N. E. Papanikolaov, *Tetrahedron Letters*, **1966**, 5445.

[10] a) H. Meerwein, V. Hederich and K. Wunderlich, *Arch. Pharm.*, **291**, 552 (1958). b) H. Meerwein, E. Betterchergm, H. Gold, E. Pfeil and G. Willfang, *J. Prakt. Chem.*, (2) **154**, 83 (1940).

[11] C. R. Johnson and D. Macants, Jr., *J. Am. Chem. Soc.*, **87**, 5406 (1965).

Table 3. The rates of S_N2 reaction of chlorophenylsulfonium perchlorates, sulfones and sulfoxides with ethoxide ion in aqueous ethanol and hydroxide ion in aqueous dimethyl sulfoxide

Compound	Solvent	Temp (°C)	(mol/sec *l*) k_2	rel. rate
	EtOH-H_2O[a)]	115±0.1	1.01×10^{-3}	1.85
	EtOH-H_2O[a)]	115±0.1	5.49×10^{-4}	1
	EtOH-H_2O[b)]	148±0.1	7.02×10^{-5}	1.9
	EtOH-H_2O[b)]	148±0.1	3.68×10^{-5}	1
	DMSO-H_2O[c)]	161±0.1	4.82×10^{-5}	1.2
	DMSO-H_2O[c)]	161±0.1	4.0×10^{-5}	1

a) The volume ratio of ethanol and water in the reaction is 4 : 3.
b) The volume ratio of ethanol and water in the reaction is 7 : 3.
c) The volume ratio of DMSO and water in the reaction is 7 : 3.

tetrahydrofuran (60 m*l*) below −5°C with vigorous stirring. After the addition was over, the solution was stirred further for 30 min and then allowed to stand at room temperature overnight. The mixture was hydrolyzed with 0.5 N hydrobromic acid solution, extracted with chloroform four times, and then dried over calcium chloride. Evaporation of chloroform followed by recrystallization of the residue from acetone-chloroform mixture gave 8.7 g (59%) of colorless *p*-chlorophenyldiphenylsulfonium bromide. Mp 221—222°C. Found: C, 57.63; H, 4.10%. Calcd for $C_{18}H_{14}ClBrS$: C, 57.4: H, 3.72%. When a sodium perchlorate solution was added to a hot solution of *p*-chlorophenyldiphenylsulfonium bromide, colorless crystals of the corresponding sulfonium perchlorate salt appeared immediately, which was collected and recrystallized from ethylene chloride-ether, Mp 160—161°C. Found: C, 54.71; H, 3.65%. Calcd for $C_{18}H_{14}Cl_2O_4S$: C, 54.5; H, 3.52%.

The *o*- and *m*-isomers were similarly prepared from the corresponding *o*- and *m*-chlorophenylphenylethoxysulfonium tetrafluoroborate which were obtained from the corresponding sulfoxides, the Meerwein salt and phenylmagnesium bromide. Both *o*- and *m*-isomers were recrystallized from chloroform-acetone-ether.

o-Isomer: Mp 147—148°C. Found: C, 54.8; H, 3.70%. Calcd for $C_{18}H_{14}Cl_2O_4S$: C, 54.5; H, 3.52%.

m-Isomer: Mp 118—120°C. Found: C, 55.01; H, 3.80%. Calcd for $C_{18}H_{14}Cl_2O_4S$: C, 54.5; H, 3.52%.

Triphenylsulfonium and Tritolylsulfonium Halide. Diphenylethoxysulfonium tetrafluoroborate prepared from diphenyl sulfoxide (9.4 g) and triethyloxonium tetrafluoroborate (10 g) was added to phenylmagnesium bromide in tetrahydrofuran below −5°C, then the reaction mixture was treated similarly to that described above, and 8 g (50%) of colorless triphenylsulfonium bromide was obtained. Mp 292—293°C (Ref.[12]) Mp 291—292°C); perchlorate; Mp 212—213°C.

Tritolylsulfonium bromide was similarly prepared from ditolylethoxysulfonium tetrafluoroborate and tolyl magnesium bromide. Mp 244—245°C.

2-Methyl-4-Chlorophenyldiphenylsulfonium Perchlorate. The titled bromide compound was prepared from 2-methyl-4-chloro-phenylphenylethoxysulfonium tetrafluoroborate obtained by reacting the corresponding sulfoxide (6 g, 0.024 mol) with triethyloxonium tetrafluoroborate (5.25 g, 0.028 mol), with the phenylmagnesium bromide (0.072 mol) as described above. The bromide salt was purified by recrystallization from acetone-ethylene chloride mixture, mp 222—223°C, yield 4.0 g (33%): 2-methyl-4-chlorophenyl-diphenylsulfonium perchlorate was quantitatively obtained by treating the corresponding sulfonium bromide with a sodium perchlorate solution. mp 193—194°C. Found: C, 55.07; H, 4.09%. Calcd for $C_{19}H_{16}O_4Cl_2S$: C, 55.5; H, 3.94%.

2-Methyl-4-Chlorophenylphenylsulfoxide and Sulfone. 2-Methyl-4-chlorophenyl phenyl sulfide, prepared by the reaction of 2-methyl-4-chlorobenzenediazonium salt with thiophenolate, was oxidized as usual with hydrogen peroxide in glacial acetic acid containing a few drops of concentrated sulfuric acid to the corresponding sulfoxide and sulfone in nearly quantitative yields and both sulfoxide and sulfone were recrystallized from benzene-petroleum ether mixture: sulfoxide, mp 39—40°C, sulfone, mp 82—83°C. Found: C, 58.70; H, 4.18%. Calcd for $C_{13}H_{11}O_2ClS$: C, 58.50; H, 4.33%.

2-Methyl-4-Chloroaniline. *o*-Methylacetoanilide

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[12] a) W. A. Bammer, *J. Am. Chem. Soc.*, **74**, 5078 (1952). b) B. S. Wildi, S. W. Taylar and H. A. Potratz, *ibid.*, **73**, 1965 (1951).

(47 g) obtained from the reaction of *o*-toluidine with acetic acid was dissolved in 70 m*l* of glacial acetic acid in a three necked flask and then liquid chlorine (14.5 g) was introduced into the flask in a sealed system which is connected with rubber tubes with vigorous stirring. After the reaction was over, the mixture was poured into a large amount of cold water, filtered, washed with cold water, recrystallized from ethanol, and 55 g of colorless crystals of 2-methyl-4-chloroacetoanilide was obtained. The amide (55 g) was hydrolyzed with hydrochloric acid in aqueous ethanol and then the salt (20 g) was treated with sodium hydroxide solution to give 2-methyl-4-chloroaniline (11 g). Bp 103—104°C/ 2 mmHg.

Chlorodiphenyl Sulfones and Chloronitrobenzenes. *o*-, *m*- and *p*-Chlorophenylphenyl sulfones were obtained by the oxidation of corresponding sulfide with hydrogen peroxide in glacial actic acid; the *o*-isomer, mp 108—109°C, the *m*-isomer, mp 113—114°C, the *p*-isomer, mp 90—91°C. Freshly distilled *o*-, *m*- and *p*-chloronitrobenzenes were used in the kinetic experiments.

Alkaline Ethanolyses of Chlorophenyldiphenylsulfonium Perchlorate. *p*-Chlorophenyldiphenylsulfonium perchlorate (1.7 g) was reacted with potassium hydroxide (0.75 g) in 6.3 m*l* of aqueous ethanol (3.6 m*l* ethanol +2.7 m*l* H_2O) at 90°C for 8 hr in an ampoule and then the mixture was poured into cold water, acidified with hydrochloric acid, extracted with chloroform 5 times and the chloroform extract was dried over calcium chloride. After chloroform was evaporated, the crystalline residue (1.2 g) was found to be the mixture of the starting sulfonium and *p*-ethoxyphenylsulfonium salt. The *p*-ethoxysubstituted sulfonium perchlorate (0.8 g) was separated by careful recrystallization with alcohol-acetone-methylene chloride mixture and finally with methylene chloride-acetone-ether. Mp 109—110°C. Found: C, 59.00; H, 4.71%. Calcd for $C_{20}H_{19}ClO_5S$: C, 58.98; H, 4.78%. The NMR charts of both *p*-chlorophenyldiphenylsulfonium perchlorate and *p*-ethoxyphenyldiphenylsulfonium perchlorate were shown in Fig. 3.

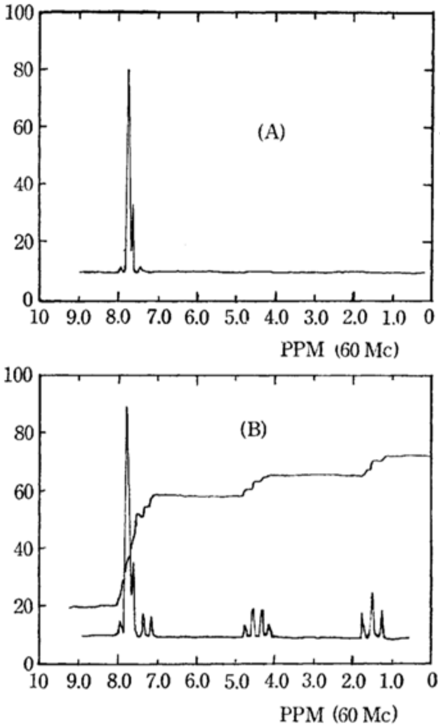

Fig. 3. NMR spectra of *p*-chlorophenyldiphenylsulfonium perchlorate (A) and *p*-ethoxyphenylsulfonium perchlorate (B).

The kinetic Experiment. Ethanol was purified first by distillation after refluxing with sodium hydroxide for 10 hr, then with magnesium ethoxide for 3 hr and again distilled. Kinetic measurements and the rate calculations of alkaline ethanolyses were carried out using the same method described in our previous work[1] by the usual Volhard method. Each run was carried out in ampoules. The concentrations of both an aryl chloride and potassium hydroxide were at around 1.3×10^{-1} N and 2.8×10^{-1} N, respectively. Kinetic measurement and the rate calculations of alkaline decomposition of the triarylsulfonium salt were performed under the same condition as in the ethanolyses, but by the use of the ultraviolet spectra of the diaryl sulfides (at $\lambda = 285$ mμ).