therefore did not examine the abilities of other steric parameters to give a better correlation between calculated and observed E values.

The present analysis shows that some consideration of both the polarizability and the size of aromatic groups is required to account for the observed E values. This conclusion is consistent with findings made with other hydrolytic enzymes,[2] e.g., α-chymotrypsin, which exhibit esterase activity. The latter enzyme has been shown to contain a hydrophobic pocket that binds to aromatic groups and to large aliphatic groups, i.e., polarizable groups.

A smaller range in E values is observed in the group of carbinols described by structure **3** than in the acyclic series. As mentioned above, the steric effects of substituents at C-2 in this group were assumed to be essentially constant. The observed variation was accounted for by the electrical parameter σ_1 and the polarizability correction associated with the number of methylene groups in the ring. Despite these simplifications, the calculated E values account for the observed differences in E values for the same substituents in the 2-substituted 1-indanols and 1-tetraols.

One of the purposes of this study was to determine whether the data collected on the hydrolysis of a number of esters could be used in conjunction with the IMF equation to separate contributions made by (a) steric effects and (b) electrical effects and the polarizability of substituents. The present results indicate that it is possible to do so, and therefore it is now also possible to predict the ee of previously unexamined esters in one of these series. Perhaps an ability to quantitatively predict the optical purities of the products of these hydrolyses in concert with an ability to predict their absolute stereochemistry will encourage others to use this microbe as a chiral reagent.

Acknowledgment. H.Z. thanks Drs. Ken-ichi Kawai, Mitsuru Imuta, and Masaji Kasai and acknowledges their contributions in the course of these studies of hydrolyses mediated by *Rhizopus nigricans*.

Reaction of Chloride Ion with Thiiranium Ions Prepared by Two Different Methods[1]

George H. Schmid,* Mark Strukelj, Snezana Dalipi, and M. Dominic Ryan

Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada

Received November 25, 1986

It has been found that the kinetically controlled product of the reaction of chloride ion with the thiiranium ion formed in the same solvent and at the same temperature by means of two different reactions is the one formed by attack at the least substituted carbon.

Thiiranium ions[2] play an important role in the chemistry of bivalent sulfur compounds. They are involved as intermediates in (i) the solvolysis of β-chloroalkyl aryl sulfides, (ii) the alkylation of thiiranes, and (iii) the addition of arene- and alkanesulfenyl halides to alkenes.[3] Reactions involving thiiranium ions as intermediates have also found synthetic utility. A number of workers[4] have demonstrated how a double bond can be functionalized in an anti stereospecific manner by means of reactions involving thiiranium ion intermediates.

Work from this laboratory has concentrated on elucidating the influence of several parameters on the mechanism of the addition of arenesulfenyl chlorides to alkenes.[5] From studies of the effect of alkene structure on the rates and products of addition, it was concluded that the first step of the addition is rate determining,[6] a fact that was later confirmed by the use of heavy atom kinetic isotope effects.[7] In the product-determining transition state, attack by chloride ion occurs at the least hindered carbon of the thiiranium ion.[8]

This last conclusion is in contrast to the reactions of stable thiiranium ions that are reported to undergo reactions with nucleophiles at the most substituted carbon.[9] While much has been made of this difference,[10] two facts must be pointed out. First, the two reactions occur under very different experimental conditions. Stable thiiranium ions are prepared in polar solvents such as liquid SO_2 at −70 to −30 °C while the addition reactions are usually

(1) Reactions of Sulfenyl Chlorides and their Derivatives. 25. Part 24: Schmid, G. H.; Garratt, D. G.; Dean, C. *Can. J. Chem.*, in press.

(2) The term thiiranium ion has been and is used to designate the positively charged three-membered sulfur-containing ring irrespective of the location of the counterion. This is analogous to the original practice of Winstein who referred to the carbocation portion of all ion pairs as varieties of carbonium ions. See: Winstein, S.; Klinedinst, P. E., Jr.; Robinson, G. C. *J. Am. Chem. Soc.* **1961**, *83*, 885.

(3) Schmid, G. H. In *Topics in Sulfur Chemistry*; Senning, A., Ed.; G. Thieme: Stuttgart, 1977; Vol. 3, p 100.

(4) (a) Trost, B. M.; Shibata, T. *J. Am. Chem. Soc.* **1982**, *104*, 3225. (b) Trost, B. M.; Shibata, T.; Martin, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 3228. (c) Caserio, M. C.; Khim, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 3231. (d) Caserio, M. C.; Fisher, C. L.; Kim, J. K. *J. Org. Chem.* **1985**, *50*, 4390.

(5) (a) Schmid, G. H.; Garratt, D. G. *Tetrahedron Lett.* **1983**, 5299. (b) Schmid, G. H.; Yeroushalmi, S.; Garrat, D. G. *J. Org. Chem.* **1980**, *45*, 910. (c) Schmid, G. H.; Garratt, D. G.; Yeroushalmi, S. *J. Org. Chem.* **1978**, *43*, 3764. (d) Schmid, G. H.; Tidwell, T. T. *J. Org. Chem.* **1978**, *43*, 460.

(6) Schmid, G. H.; Garratt, D. G. In *Chemistry of Double Bonded Functional Groups*, Supplement A, Part 2; Patai, S., Ed.; Wiley: London, 1977; Chapter 9.

(7) Kanska, M.; Fry, A. *J. Am. Chem. Soc.* **1983**, *105*, 7666.

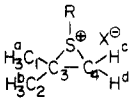
(8) Schmid, G. H.; Dean, C. L.; Garratt, D. G. *Can. J. Chem.* **1976**, *54*, 1253.

(9) (a) Gybin, A. S.; Krimer, M. Z.; Smit, W. A.; Bogdonov, B. C.; Vorob'eva, E. A. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1979**, 510. (b) Bolster, J. B.; Kellog, R. M. *J. Chem. Soc., Chem. Commun.* **1978**, 630. (c) Capozzi, G.; Lucchini, O.; Lucchini, V.; Modena, G. *Tetrahedron Lett.* **1975**, 2603.

(10) (a) Smit, W. A.; Zefirov, N. S.; Bodrikov, I. V.; Krimer, M. Z. *Acc. Chem. Res.* **1979**, *12*, 280. (b) Smit, W. A.; Zefirov, N. S.; Bodrikov, I. V. *Organic Sulfur Chemistry*; Freidlina, R. Kh., Skorova, A. E., Eds.; Pergamon: New York, 1981.

0022-3263/87/1952-2403$01.50/0

Table I. Observed NMR Spectra of Thiiranium Ion 3b



^{1}H Spectra

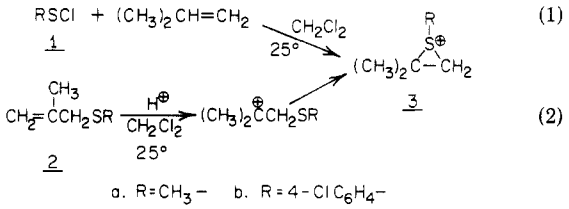
H^a	H^b	H^c	H^d	X^-	R	ref
1.58 s	1.82 s	3.62 s		$SbCl_6^-$	4-ClC_6H_4	9
1.55	1.85 s	3.80 s		$CF_3SO_3^-$	4-ClC_6H_4	this work

^{13}C Spectra

C_1	C_2	C_3	C_4	X^-	R	ref
15.0		62.4	49.5	SbF_6^-	4-ClC_6H_4	9
19.0		91.7	54.9	SbF_6	2,4,6-$(CH_3)_3C_6H_2$	9
21.9		88.0	55.0	$CF_3SO_3^-$	4-ClC_6H_4	this work

carried out in relatively nonpolar solvents such as CH_2Cl_2 at 25 °C. Second, stable thiiranium ions are frequently reacted in the presence of silver chloride, a byproduct of the formation of the thiiranium ion.[11]

These differences are not trivial and may have an effect on either the position of attack of the nucleophile on the ion or may cause subsequent isomerization of the adducts.[12] In order to evaluate these differences, we have studied the reaction of structurally similar thiiranium ions formed in the same solvent and at the same temperature by means of the two reactions shown in eq 1 and 2.



a. R=CH_3– b. R=4-ClC_6H_4–

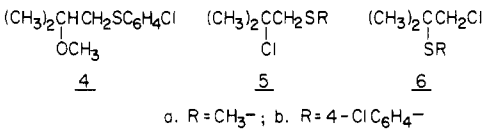
The first reaction (eq 1) is the addition of methane- (**1a**) or 4-chlorobenzenesulfenyl chloride (**1b**) to methylpropene, a reaction that is known to involve a thiiranium ion intermediate.[3] The second reaction (eq 2) is the preparation of a thiiranium ion by the addition of acid to methyl-3-(methylthio)propene (**2a**) or methyl-3-[(4-chlorophenyl)thio]propene (**2b**). The rate-determining step in this reaction is the transfer of a proton to the alkene to form a β-arylthio carbocation,[13] which immediately closes to form a thiiranium ion.

The purpose of this work is to determine whether there is a difference in the site of attack by chloride ion on the same thiiranium ion formed by two different reactions in the same homogeneous medium and at the same temperture. This paper reports the results of this investigation and its mechanistic implications.

Results

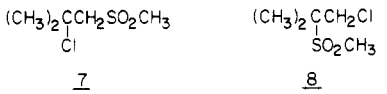
Dissolving **2b**, prepared by the reaction of sodium 4-chlorothiophenoxide and methallyl chloride in methanol, in hexane and adding the resultant solution slowly to trifluoromethanesulfonic acid (triflic acid) formed the stable ion **3b**. The thiiranium ion is not soluble in hexane and forms a distinct phase between the hexane layer and the triflic acid layer. The presence of the ion in this layer was confirmed by its NMR given in Table I. For comparison, the NMR of the same ion prepared by other workers is included in Table I. Attempts to prepare the ion by adding neat **2b** to triflic acid were unsuccessful because the ion once formed reacts with the starting alkene.

This identity of the ion was further confirmed by its reaction with nucleophiles. Thus addition of the layer containing **3b** to methanol containing an excess of sodium bicarbonate or urea formed **4** as the only product. The identical result is reported by Oki.[14] Reaction of the layer containing **3b** with a solution of tetraethylammonium chloride in dichloromethane at 25 °C containing a fivefold excess of urea formed a mixture of **5b** and **6b**. The relative proportions of **5b** and **6b** depend on the time the products remain in the reaction mixture before workup. The ratio **5b/6b** is 0.53 if workup is started immediately after the addition of chloride ion. Under these conditions, **6b**, the product of chloride attack at the least hindered carbon of the ion, is formed preferentially. The ratio **5b/6b** is 1.87 if the reaction mixture is allowed to stand for 5 min before workup. Now the product present in greatest amount is the one of attack at the most hindered carbon of the ion. These data are consistent with acid-catalyzed isomerization of the kinetically controlled product composition, a well-known reaction.[15] No isomerization occurs during workup as shown by control experiments.



a. R=CH_3–; b. R=4-ClC_6H_4–

Similar results are obtained by reacting **2a** with a saturated solution of HCl in dichloromethane at 25 °C. The addition of HCl to **2a** is very slow, much slower than the acid-catalyzed isomerization of **6a**. As a result, the product composition changes with time. The initial product composition was determined by removing aliquots at timed intervals during the first 10% of the reaction. The aliquots were immediately treated with *m*-chloroperbenzoic acid to oxidize the products **5a** and **6a** to their corresponding sulfones **7** and **8**.



The quantities of each sulfone, which do not isomerize, were determined by GLC. Plots of the percent **8** with time are linear for the first 800–1000 s of reaction. At longer times, the points deviate noticeably from a straight line. The linear portions of six independently determined plots were extrapolated to zero time to give an initial composition of 96 + 4% **8**. Again, initial chloride attack at the least hindered carbon atom of the thiiranium ion is favored.

Discussion

The results of the four experiments are summarized in Table II. Experimental conditions are not identical, despite use of the same solvent and temperature. The difference is the presence of triflic acid in the solution used to prepare the ions from **3a** and **3b**. This changes the medium slightly and causes the rapid isomerization of the product. This accounts for the differences in the initial product composition. Despite this, it is clear that, in all cases given in Table II, attack by chloride ion at the least hindered carbon atom of the thiiranium ion is the preferred

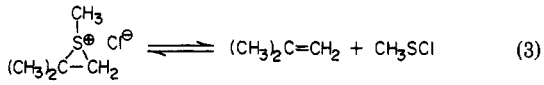
(11) Gybin, A. S.; Smit, V. A.; Bogdanov, V. S.; Krimer, M. Z. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1978**, 2156.
(12) For a review of metallic ion assistance to ionization see: Rudakov; Kozhevnikov; Zamashchikov, *Russ. Chem. Rev.* **1974**, *43*, 305.
(13) Reference 6, p 732.
(14) Oki, M.; Nakanishi, W.; Fukunaga, M. *Chem. Lett.* **1975**, 1277.
(15) Mueller, W. H.; Butler, P. E. *J. Org. Chem.* **1967**, *32*, 2925.

Table II. Kinetic Products of Reaction of Chloride Ion with Thiiranium Ions 3a and 3b Prepared by Different Reactions

reaction	R	product, % $(CH_3)_2CCH_2Cl$ (SR)	product, % $(CH_3)_2CCH_2SR$ (Cl)
$(CH_3)_2C{=}CH_2$ + RSCl	CH_3	95 ● 2	4 ± 2
	4-ClC_6H_4	88 ± 2	11 ± 2
$CH_2{=}C(CH_3)CH_2SR$ + CF_3SO_3H	4-ClC_6H_4	65 ± 2	35 ± 3
$CH_2{=}C(CH_3)CH_2SR$ + HCl	CH_3	96 ± 4	

path for reaction in dichloromethane.

It is possible to explain the results of the reactions of ions **3a** and **3b** given in Table II in another way. Thus, chloride ion could react with the thiiranium ion at sulfur. This known reaction,[16] shown in eq 3 for **3a**, results in the

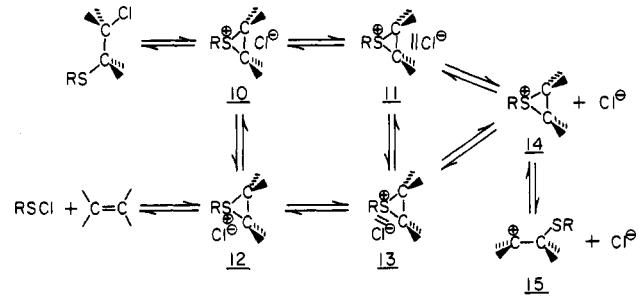


$$\underset{\textbf{3a}}{(CH_3)_2C(CH_2)S^{\oplus}(CH_3)Cl^{\ominus}} \rightleftharpoons (CH_3)_2C{=}CH_2 + CH_3SCl \qquad (3)$$

formation of methylpropene and methanesulfenyl chloride. If this were the main reaction of the stable thiiranium ion **3a** and chloride ion, then it would be essentially the same as the reaction of methanesulfenyl chloride and methylpropene. Consequently the same product mixture would be expected from both reactions. To check this possibility, the reaction of **2a** in a saturated solution of HCl in dichloromethane was carried out in the presence of a fivefold excess of 2,3-dimethyl-2-butene. If methanesulfenyl chloride is formed, it will add to 2,3-dimethyl-2-butene 10 times faster than to methylpropene.[17] As a result, substantial quantities of 2-chloro-3-(methylthio)-2,3-dimethylbutane (**9**), the adduct of 2,3-dimethyl-2-butene and methanesulfenyl chloride, would be formed. The reaction was carried out and analyzed as previously described. The amount of **9** formed in this reaction was found to be 4.9 ± 0.8% on the basis of the average of eight independent analysis. Therefore, we can conclude that attack at sulfur of the thiiranium ion by chloride ion does occur, but it is a minor reaction that does not account for the similarity in the product composition of the two reactions.

Stable thiiranium ions are reported to react with nucleophiles in polar solvents at the more substituted carbon atom.[10] This result is contrary to our findings reported in Table II for the reaction of ions **3a** and **3b** in dichloromethane, a less polar solvent. One possible explanation for the effect of polar and nonpolar solvents on the site of chloride attack at thiiranium ions may be that different types of ions or ion pairs are involved in the different solvents. The importance of ion pairs in the mechanism of many reactions in solution is well documented;[18] electrophilic additions are no exception. A number of people have proposed that the mechanism of an electrophilic addition reaction could involve ion-pair intermediates.[19] Subsequent work by Yates[20] and Dubois[21]

Scheme I



established the importance of ion pairs in the bromination of alkenes. In 1973, Fitzgerald provided evidence that the mechanism of the electrophilic addition of arenesulfenyl chlorides to alkenes and the mechanism of neighboring sulfur participation in the reaction of beta chloroalkyl aryl sulfides both involve the same series of thiiranium ions.[22] The major features of the mechanism that we proposed are shown in Scheme I.[3] The upper sequence of reactions involving ion pairs **10**, **11**, and **14** is the general solvolysis scheme proposed by Winstein.[23] The lower sequence of reactions is similar to that proposed by Poutsma.[19] Ion pairs **10** and **12** are contact ion pairs, and **11** and **13** are solvent-separated ion pairs that differ only in the location of the counterion. Our contribution to this mechanism was to link these two paths directly between ion pairs **10**–**12** and **11**–**13** or by means of the dissociated ion **14**. We propose in this scheme that electrophilic addition of arenesulfenyl chlorides to alkenes, isomerization of the Markovnikov–anti-Markovnikov adducts, and solvolysis of β-chloroalkyl aryl sulfides all occur by means of a common mechanism.[3]

Not included in our original proposal is the open β-arylthio carbocation **15**. Evidence for inclusion of such an open ion comes from the fact that the reaction of 2,4-dinitrobenzenesulfenyl chloride and 1-(4-methoxyphenyl)-propene forms products of regiospecific and nonstereospecific addition.[24] In addition, stable thiiranium ions also form open β-arylthio carbocations. Thus, the thiiranium ion prepared by the addition of tris(4-chlorophenyl)-sulfonium hexachloroantimonate to (*Z*)-1-phenylpropene in dichloromethane at −70 °C according to the method of Modena[25] reacts with chloride ion to form products whose stereochemistry changes with time.[26] Thus, at short reaction times, the product is formed via a thiiranium ion while at longer reaction times the thiiranium ion forms an open β-arylthio carbocation that is the precursor of the reaction products.

We can conclude from this last fact that thiiranium ions formed under stable conditions have pathways to products unavailable to the structurally similar thiiranium ions formed in the addition of sulfenyl chlorides to alkenes. These alternate pathways seem to become more important as the solvent polarity increases. Therefore, it is possible that the increased amount of product of chloride attack at the more hindered carbon of **3** in polar solvents may be due to the formation of the open aryl or β-alkylthio car-

(16) (a) Schmid, G. H.; Fitzgerald, P. H. *J. Am. Chem. Soc.* **1971**, *93*, 2547. (b) Owsley, D. C.; Helmkamp, G. K.; Spurlock, S. N. *J. Am. Chem. Soc.* **1969**, *91*, 3606.
(17) Schmid, G. H.; Garratt, D. G. *Can. J. Chem.* **1973**, *51*, 2463.
(18) Gordon, J. E. *The Organic Chemistry of Electrolyte Solutions*; Wiley: New York, 1975.
(19) (a) de la Mare, P. B. D.; Klassen, N. V.; Koenigsberger, R. *J. Chem. Soc.* **1961**, 5285. (b) Cabaleiro, M. C.; Johnson, M. D. *J. Chem. Soc. B* **1967**, 565. (c) Poutsma, M. L.; Kartch, J. L. *J. Am. Chem. Soc.* **1965**, *89*, 6595.
(20) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1477.
(21) Garnier, F.; Dubois, J. E. *Bull. Soc. Chim. Fr.* **1968**, 3797.
(22) Fitzgerald, P. H. Ph.D. Thesis, University of Toronto, 1973; *Diss. Abstr.* **1973**, *34*, 4855.
(23) For a summary and complete references to Winstein's work on ion pairs see: Bartlett, P. D. *J. Am. Chem. Soc.* **1972**, *94*, 2161.
(24) Schmid, G. H.; Nowlan, V. J. *J. Org. Chem.* **1972**, *37*, 3086.
(25) Capozzi, G.; De Lucchi, O.; Lucchini, V.; Modena, G. *Tetrahedron Lett.* **1975**, 2603.
(26) Schmid, G. H.; Macdonald, D. I. *Tetrahedron Lett.* **1984**, 157.

bocation. Work is currently under way in our laboratory to test this hypothesis.

In summary, we have studied the reaction of chloride ion and a thiiranium ion prepared two different ways in dichloromethane at 25 °C. The first method is by the addition of either methane- or 4-chlorobenzenesulfenyl chlorides to methylpropene. The second method is by the reaction of triflic acid and either methyl-3-(methylthio)-propene or methyl-3-[(4-chlorophenyl)thio]propene. The kinetically controlled product in the reaction of each thiiranium ion with chloride ion is the one formed by attack at the least substituted carbon.

Experimental Section

All melting points are uncorrected. ^{1}H NMR were recorded on Varian T-60, XL-100, or XL200 spectrometers. ^{13}C NMR spectra were recorded on Varian CFT-20 (20-MHz) and XL-100 (25-MHz) spectrometers. All chemical shifts are relative to Me_4Si. IR spectra were recorded on Pye Unicam SP3-200 and Sp1025 and Perkin-Elmer 337 grating spectrometers. UV–visible spectra were recorded on a Unicam SP800A UV–visible spectrometer. Gas–liquid chromatography was carried out on a Varian 2700 aerograph equipped with a flame ionization detector using a Varian CDS 111 digital integrator to obtain peak areas. Analysis was carried out with a 5% QF-1 on Chromosorb in a 2 m × 2 mm silanized glass column at 120 °C with a flow rate of 24 mL/min.

All solvents used were ACS grade. Dichloromethane was further purified by distillation after refluxing over P_2O_5. Tetrahydrofuran was purified by distillation after refluxing over sodium benzophenone ketyl, and methanol was purified by distilling from magnesium turnings. All solvents were shielded from light and stored over 3-Å molecular sieves that had been activated by heating at 220–300 °C for 8–12 h. All inert-atmosphere work was carried out under argon.

Methanesulfenyl chloride was prepared by reacting 1 equiv of dimethyl sulfide with 1 equiv of sulfuryl chloride at −70 °C in an inert atmosphere. The resultant solution of methanesulfenyl chloride was distilled from the SO_2 formed as a byproduct. Solutions of methanesulfenyl chloride in dichloromethane were prepared by distilling methanesulfenyl chloride directly into a preweighed volumetric flask half-filled with solvent. The final concentration of methanesulfenyl chloride was determined iodometrically by the method of Kharasch and Wald.[27]

2-Methyl-3-(methylthio)propene (2a). A solution of methanethiol (5.08 g, 106 mol) in dry tetrahydrofuran (10 mL) cooled to −20 °C was added to sodium hydride (4.419 g, 0.104 mol, 57% oil dispersion; washed three times with 10 mL of pentane and pumped dry) in dry tetrahydrofuran (10 mL) at 0 °C. After the mixture was stirred for 60 min at 0 °C, 2-methyl-3-chloropropene (9.0 g, 0.10 mol) in dry tetrahydrofuran (10 mL) was added dropwise. The reaction mixture was stirred as it warmed to room temperature. After 30 min, the reaction mixture was filtered and distilled through a 30-cm spinning band fractionation column to give 6.12 g (0.060 mol) of product: bp 108–110 °C; ^{1}H NMR ($CDCl_3$) δ 1.80 (s, 3 H), 1.91 (s, 3 H), 3.06 (s, 2 H), 4.83, 4.78 (7, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.4, 20.5, 41.5, 40.9, 113.1. Anal. Calcd for $C_5H_{10}S$: C, 58.79; H, 9.79. Found: C, 59.03; H, 9.62.

2-Methyl-3-(methylsulfonyl)propene. A solution of *m*-chloroperoxybenzoic acid (231 mg, 1.32 mmol) in dry dichloromethane (10 mL) was added to a solution of **2a** (61 mg, 0.60 mmol) in 2 mL of dichloromethane at room temperature. The reaction mixture was allowed to stand for 15 min and then was washed with a saturated aqueous solution of $NaHSO_3$ until a negative starch/iodine test was obtained. The organic layer was washed twice with 20 mL of saturated aqueous $NaHCO_3$ solution and once with 20 mL of saturated aqueous NaCl solution and dried over $MgSO_4$. The solvent was removed by rotary evaporation to give 72 mg (91% yield) of product: mp 39–40 °C; ^{1}H NMR ($CDCl_3$) δ 1.97 (m, 3 H), 2.88 (s, 3 H), 3.68 (s, 2 H), 4.08 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.0, 38.8, 62.3, 138.9, 120. Anal. Calcd for $C_5H_{10}SO_2$: C, 44.77; H, 7.46. Found: C, 44.86; H, 7.51.

(27) Kharasch, N.; Wald, M. *Anal. Chem.* **1955**, *27*, 996.

3-Chloro-2,3-dimethyl-2-(methylsulfonyl)butane. A solution of 0.937 g (0.0114 mol) of methanesulfenyl chloride in 25 mL of dichloromethane was added dropwise to a cooled solution (−35 °C) of 2,3-dimethyl-2-butene in 10 mL of dichloromethane. To the reaction mixture was then added 4.14 g (0.024 mol) of *m*-chloroperoxybenzoic acid dissolved and suspended in 25 mL of dichloromethane. The reaction mixture was allowed to warm to room temperature, and the product was isolated by the procedure given for 2-methyl-3-(methylsulfonyl)propene to give 1.76 g (78% yield) of product, mp 97–99 °C dec after recrystallization from acetone/hexane. Because the solid readily eliminates HCl, analytical samples could not be prepared: ^{1}H NMR ($CDCl_3$) δ 1.88 (s, 6 H), 1.60 (s, 6 H), 2.98 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 30.3, 39.4, 20.7, 75.2, 70.1.

2-Chloro-2-methyl-1-(methylsulfonyl)propane (7) and 1-Chloro-2-methyl-2-(methylsulfonyl)propane (8). To a solution containing 75% **5a** and 25% **6a** (determined by NMR) in 20 mL of dichloromethane was added 2.2 equiv of *m*-chloroperoxybenzoic acid as a saturated solution in dichloromethane at room temperature. After workup by the procedure given for 2-methyl-3-(methylsulfonyl)propene, the reaction mixture was analyzed by GLC. The retention times for each isomer were determined by oxidizing several mixtures of **5a** and **6a**, each containing different **5a**/**6a** ratios. Correlation of the starting percent **5a** and **6a** and the percent of the corresponding sulfones determined by ^{1}H NMR established the following retention times: **7**, 20.7 min; **8**, 22.7 min. ^{1}H NMR ($CDCl_3$): (**7**) δ 1.84 (s, 6 H), 3.04 (s, 3 H), 3.53 (s, 2 H); (**8**) 1.50 (s, 6 H), 2.93 (s, 3 H), 3.82 (s, 2 H).

Addition of HCl to 2a without Added 2,3-Dimethyl-2-butene. A solution of 250 mg (2.45 mmol) of **2a** in dichloromethane and 10 mL of a saturated solution of HCl in dichloromethane (0.24 M) were equilibrated in a thermostated bath at 25 ± 0.05 °C for 30 min and then combined and made up to 25 mL with dichloromethane in a volumetric flask. Aliquots (4 mL) were removed at time intervals by pipet, oxidized with *m*-chloroperoxybenzoic acid, and analyzed by GLC. The GLC tracing showed peaks for **7**, **8**, and another peak at 14 min due to 2-methyl-3-(methylsulfonyl)propene.

Addition of HCl to 2a with Added 2,3-Dimethyl-2-butene. The reaction was carried out in the same way as without added 2,3-dimethyl-2-butene except that 1.012 g (12.02 mmol) of 2,3-dimethyl-2-butene was added to the reaction mixture. The GLC tracing showed peaks for **7**, **8**, 2-methyl-3-(methylsulfonyl)propene, tetramethylethylene oxide, and 3-chloro-2,3-dimethyl-2-(methylsulfonyl)butane.

Methyl-3-[(4-chlorophenyl)thio]propene. To a mixture of 5.4 g (0.130 mol) of NaH in 10 mL of dried tetrahydrofuran cooled to 0 °C was added dropwise a solution of 18.7 g (0.130 mol) of 4-chlorobenzenethiol in 10 mL of tetrahydrofuran while the temperature was maintained at 0 °C. Then, a solution of 9.0 g (0.10 mol) 3-chloro-2-methylpropene in 10 mL of tetrahydrofuran was added dropwise. The reaction mixture was allowed to stir overnight at room temperature. To the reaction mixture was added 50 mL of water followed by 50 mL of chloroform. The organic layer was separated and washed three times with 50 mL of dilute sodium hydroxide followed by three washing with 50 mL each of water. The solvent was removed by rotary evaporation. Distillation gave 12.8 g (65% yield) of product: bp 68–72 °C (0.4 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.88 (s, 3 H), 2.53 (s, 2 H), 4.82 (s, 2 H), 7.25 (s, 4 H). Anal. Calcd for $C_{10}H_{11}SCl$: C, 60.45; H, 5.54. Found: C, 60.49; H, 5.51.

Thiiranium ion 3a was prepared by placing 30 drops of trifluoromethanesulfonic acid in one container and 16 drops of **2a** dissolved in 16 drops of hexane in another container. Both containers were under argon and cooled to 0 °C. The solution of **2a** in hexane was slowly added to the triflic acid by means of a pipet. The resulting solution was gently shaken by hand and placed in ice intermittently. A three-phase system quickly developed. On the basis of NMR analysis, the top layer contains unreacted **2a** in hexane. The yellow and viscous middle layer contains the ion **3a**, and the triflic acid was in the bottom layer. The top layer was completely removed by means of a pipet, and the middle was used in subsequent reactions.

Reaction of 3a with Tetraethylammonium Chloride. Ion **3a** prepared as described above was injected into a solution of

0.34 g (4.0 mmol) of $NaHCO_3$ and 0.28 g (1.5 mmol) of tetraethylammonium chloride in 30 mL of dry dichloromethane. The reaction was immediately quenched by the addition of 30 mL of water. The layers were separated, and the organic layer was washed three times with 20 mL of water. The organic layer was dried over $MgSO_4$ and filtered and the solvent removed by rotary evaporation. The residue was dissolved in $CDCl_3$ and analyzed by NMR.

Acknowledgment. Financial assistance by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Vastly Improved Para Preference in the Nitration of Halobenzenes

Pierre Laszlo* and Pascal Pennetreau

Institut de Chimie Organique (B6), Université de Liège, Sart-Tilman par 4000 Liège, Belgium

Received February 2, 1987

The halobenzenes are mononitrated with cupric nitrate supported on the K10 montmorillonite in the presence of acetic anhydride, in hexane, or in methylene chloride, at room temperature or below. Good isolated yields (50–75%) are accompanied by much improved para selectivities, up to a para-to-ortho ratio of 35 (a selectivity factor of 70) for fluorobenzene. The observed selectivity factors are determined uniquely by the polarizability of the halogen substituent.

Most aromatic nitrations, as classically performed with mixtures of nitric and sulfuric acids, give predominantly ortho and para products. Quite often their distribution is close to the statistical 2:1 ratio.[1] Yet it is desirable to improve the regioselectivity, pushing it toward a higher proportion of the para product. Our start in this direction was nitration of phenols by "clayfen",[2] i.e., clay-supported ferric nitrate. It gave significantly greater para/ortho ratios than other procedures.[3] We address now a similar goal for the converse case of aromatic systems deactivated by electron-withdrawing substituents, the halobenzenes.

This work is part of a more general program for renovating the important reactions of organic chemistry, using silicates as supports and catalysts.[4] For this purpose we bring to bear principles and rules of physical chemistry. The present advance is based on the simple notions of charge control and of the electrostatic interaction of a charge with a polarizable distribution. From such conceptual simplicity, one can learn how to master the reaction outcome. Thus, it becomes easy to steer it to the formation of the most desirable product, under the gentlest of conditions.

Table I. Product Distribution in the Nitration of Halobenzenes[1a]

substrate	product		
	ortho	meta	para
fluorobenzene	12		87
chlorobenzene	30	0.9	69
bromobenzene	37	1.2	62
iodobenzene	38	1.8	60

1. Background

Halobenzenes are deactivated for electrophilic aromatic substitution, they react slower than benzene. Nevertheless, the halogen substituents are ortho–para directing.[1] The explanation given to this paradox (or Holleman anomaly[1a]) invokes the Hammond postulate to assume that the transition state resembles the Wheland (arenium ion) intermediate.[5] The arenium ions conducive to ortho or para products are stabilized by delocalization of the lone pairs from the halogen substituents.[6] The observed para preference, according to this interpretation, stems from the greater contribution of para-quinonoid as compared to ortho-quinonoid limiting forms, in the resonance description.[5] The proportion of para product is the highest for fluorobenzene and the smallest for iodobenzene.[7] This is interpreted by greater relative deactivation due to the inductive effect of the substituent at the ortho than at the more remote para position, in consonance with fluorine

(1) (a) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*; Cornell University Press; Ithaca, New York, 1953; pp 256–69. (b) Brown, H. C.; Bonner, W. H. *J. Am. Chem. Soc.* **1954**, *76*, 605–606. (c) Coombes, R. G.; Crout, D. G. H.; Hoggett, J. G.; Moodie, R. B.; Schofield, K. *J. Chem. Soc. B* **1970**, 347–357.

(2) Cornélis, A.; Laszlo, P. *Synthesis* **1985**, 909–918.

(3) Cornélis, A.; Laszlo, P.; Pennetreau, P. *Clay Miner.* **1983**, *18*, 437–445. Cornélis, A.; Laszlo, P.; Pennetreau, P., *Bull. Soc. Chim. Belg.* **1984**, *93*, 961–972.

(4) Oxidation of Alcohols into Carbonyls: Cornélis, A.; Laszlo, P. *Synthesis* **1980**, 849–850. Preparation of Symmetrical Formaldehyde Acetals: Cornélis, A.; Laszlo, P. *Synthesis* **1982**, 162–163. Preparation of Nitrites: Cornélis, A.; Herzé, P. Y.; Laszlo, P. *Tetrahedron Lett.* **1982**, *23*, 5035–5038. Oxidative Coupling of Thiols: Cornélis, A.; Depaye, N.; Gerstmans, A.; Laszlo, P. *Tetrahedron Lett.* **1983**, *24*, 3103–3106. Nitration of Phenols: Cornélis, A.; Laszlo, P.; Pennetreau, P. *J. Org. Chem.* **1983**, *48*, 4771–4772; *Bull. Soc. Chim. Belg.* **1984**, *93*, 961–972. Diels-Alder: Laszlo, P.; Lucchetti, J. *Tetrahedron Lett.* **1984**, *25*, 1567–1570; **1984**, *25*, 2147–2150; **1984**, *25*, 4387–4388. Regeneration of Carbonyls: Laszlo, P.; Polla, E. *Tetrahedron Lett.* **1984**, *25*, 3309–3312; *Synthesis* **1985**, 439–440. Balogh, M.; Cornélis, A.; Laszlo, P. *Tetrahedron Lett.* **1984**, *25*, 3313–3316. Laszlo, P.; Pennetreau, P.; Krief, A., *Tetrahedron Lett.*, **1986**, *27*, 3153-54; Preparation of Azides: Laszlo, P.; Polla, E. *Tetrahedron Lett.* **1984**, *25*, 3701–3704. Preparation of Iminophosphoranes: Laszlo, P; Polla, E. *Tetrahedron Lett.* **1984**, *25*, 4651–4654. Aromatization of Dihydropyridines: Balogh, M.; Hermecz, I.; Mészáros, Z.; Laszlo, P. *Helv. Chim. Acta* **1984**, *67*, 2770–2772. Michael: Laszlo, P.; Pennetreau, P. *Tetrahedron Lett.* **1985**, *26*, 2645–2648. Knoevenagel Condensation: Chalais, S.; Laszlo, P.; Mathy, A. *Tetrahedron Lett.* **1985**, *26*, 4453–4454. Friedel-Crafts: Chalais, S.; Cornélis, A.; Gerstmans, A.; Kołodziejski, W.; Laszlo, P.; Mathy, A.; Mětra, P. *Helv. Chim. Acta* **1985**, *68*, 1196–1203. Protective Tetrahydropyranylation of Alcohols: Hoyer, S.; Laszlo, P.; Orlović, M.; Polla, E. *Synthesis* **1986**, 655–657. Gattermann Synthesis of Olefins: Baran, J.; Laszlo, P. *Tetrahedron Lett.* **1985**, *26*, 5135–5136. Dienone-Phenol Rearrangement: Chalais, S.; Laszlo, P.; Mathy, A., *Tetrahedron Lett.* **1986**, *27*, 2627–2630.

(5) March, J. *Advanced Organic Chemistry. Reactions, Mechanisms, and Structure*, 2nd ed.; *McGraw-Hill: New* York, 1977; Chapter 11. Stock, L. M. *Prog. Phys. Org. Chem.* **1976**, *12*, 21–47.

(6) Even fluorine can stabilize incipient positive charge in an electrophilic substitution: Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley-Interscience: New York, 1973; p 73.

(7) Holleman, A. F. *Chem. Rev.* **1924**, *1*, 187–229.

0022-3263/87/1952-2407$01.50/0