Linear Free-Energy Relationships in Electrophilic Addition Reactions of Alkenes. Use of Addition of Arenesulfenyl Chloride and Hydration as Mechanistic Models of Bromination[1]

George H. Schmid* and Thomas T. Tidwell

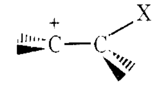
Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada

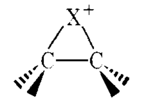
Received April 21, 1977

The use of the structure–reactivity profiles of the addition of arenesulfenyl chloride and hydration of alkenes are proposed as models of reactions involving bridged and open-ion-like rate-determining transition states, respectively. Using these reactions as standards, it is possible to obtain information on the structure of the rate-determining transition states of other electrophilic addition reactions. This method is illustrated by applying it to the electrophilic bromination of alkenes.

Linear free-energy relationships have been used frequently in studies of the mechanisms of organic reactions.[2] For electrophilic addition reactions, Hammett correlations have been the most successful of such relationships.[3] Use of the Taft correlation for electrophilic additions to alkyl-substituted ethylenes has been less successful. In general, as the number of alkenes to be correlated and their structural complexity increases, such correlations become increasingly unsatisfactory.[4] Attempts to improve the Taft correlation by defining a new substituent steric parameter, E_s^*,[5] or by introducing multiple parameters[6] have not been particularly successful. Thus far, linear free-energy relationships have been of limited use in establishing the structure of the rate-determining transition states of electrophilic addition reactions.

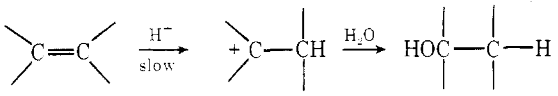
The fundamental problem is that there are more variables affecting the structure of the rate-determining transition state of electrophilic additions than in the reactions defining the Taft substituent constants. For example, the transition states of electrophilic additions may vary from those resembling an open ion 1 to those resembling a bridged ion 2. Clearly one set of substituent steric and polar parameters is inadequate, since the effects of substitutents in these two transition states are different. Also, the ground and transition states of these reactions may be affected by such variables as intra- and intermolecular steric effects, solvent effects, and electronic effects in ways that differ from those for which the substituent constants are defined.

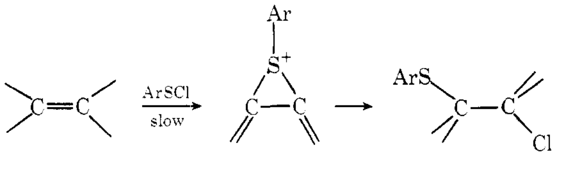

1


2

One solution to this problem is to choose reactions to serve as models of the structure reactivity relationship for the two extreme mechanisms proceeding through transition states 1 and 2. These reactions then become the standards against which the structure–reactivity relationship of other electrophilic addition reactions can be compared. In this way, it should be possible to establish if the rate-determining transition state for a particular reaction more closely resembles structure 1 or 2.

The following reactions have been chosen as models. Protonation of alkenes in acid-catalyzed hydrations has been established to proceed by an open ion through the entire range of reactivity and is the best example of the first class of reaction.[3a,7] The addition of sulfenyl halides to alkenes is a reaction which proceeds through a bridged transition state for the entire range of reactivity and is the best example of the second category. The mechanism of the hydration reaction is supported by the correlation of rates with structure, solvent isotope effects, acidity dependence, and other kinetic criteria.[3a,7] The mechanism of sulfenyl halide addition is securely based on rate–structure correlations, product stereochemistry, and direct observation of thiiranium ions.[7]





A reaction suitable for study by this method is bromination. This is a reaction which has received an enormous amount of attention. While its mechanism is reasonably well established, there is still some ambiguity regarding its rate-determining transition-state structure.

Results and Discussion

The rate constants of acid-catalyzed hydration ($k_2^{\mathrm{H^+}}$), bromination in methanol containing 0.2 M NaBr ($K_g^{\mathrm{Br_2}}$), and addition of 4-chlorobenzenesulfenyl chloride in 1,1,2,2-tetrachloroethane (k_2^{ArSCl}) for a group of alkenes of representative structural types are given in Table I. The second-order rates of hydration were obtained by dividing the observed rates extrapolated to $H_0 = 0$ by the acidity function h_0 for that acidity.[3a–c] The second-order rates of bromination are actually a mixture of two terms: the usual second-order term, first order in both alkene and bromine, and a third-order term, first order in alkene, bromine, and bromide ion. Under the experimental conditions, the term involving bromide ion is kinetically unimportant despite its large concentration in solution.[8] Thus, $k_g^{\mathrm{Br_2}}$ reflects the effect of alkene structure on the second-order term.

In Figure 1, log $k_2^{\mathrm{H^+}}$ is plotted against log $k_g^{\mathrm{Br_2}}$. While the points can be fitted to a line, the correlation is poor. Rather than defining one line, the points are grouped into two regions. One group of alkenes, which forms tertiary carbonium ions, is found between the values of −3 and −4 for log $k_2^{\mathrm{H^+}}$, while the other group, which forms secondary carbonium ions, is found between the values of −6 and −7.6. Even within these groups, there does not appear to be a direct correspondence between reactivity in bromination and reactivity in hydration. Ethylene (**3**), which has been proposed to form the primary ethyl carbonium ion,[3b] falls outside both of these groups. It is thus clear from Figure 1 that there is no similarity in the structure–reactivity profiles of hydration and bromination of alkenes. Therefore, the rate-determining transition states for the bromination of the compounds in Figure 1 do not resemble an open-ion structure throughout the range of reactivity.

0022-3263/78/1943-0460$01.00/0

Table I. Rates of Hydration, Bromination, and Addition of 4-Chlorobenzenesulfenyl Chloride[j] to Alkenes at 25 °C

Alkene	Registry no.	Compd no.	k_2^{ArSCl},[a] $M^{-1} s^{-1}$	$k_g^{Br_2}$,[b] $M^{-1} s^{-1}$	$k_2^{H^+}$,[c] $M^{-1} s^{-1}$
$CH_2=CH_2$	74-85-1	**3**	65	0.505	0.15×10^{-1}[d]
$CH_3CH=CH_2$	115-07-1	**4**	205	30.7	0.238×10^{-8}
$EtCH=CH_2$	106-98-9	**5**	248	48.3	
i-$PrCH=CH_2$	563-45-1	**6**	140	28.3	
t-$BuCH=CH_2$	558-37-2	**7**	95	13.4	
n-$BuCH=CH_2$	592-41-6	**8**	133	31.7	0.432×10^{-8}
$(CH_3)_2C=CH_2$	115-11-7	**9**	550	2 730	0.37×10^{-3}
$(Et)_2C=CH_2$	760-21-4	**10**	372	4 500	
$(t\text{-}Bu)_2C=CH_2$	5857-68-1	**11**	3.17×10^{-2}	12.8	
$Et(CH_3)C=CH_2$	563-46-2	**12**	611	4 470	0.522×10^{-3}
i-$Pr(CH_3)C=CH_2$	563-78-0	**13**	420	1 620	
t-$Bu(CH_3)C=CH_2$	594-56-9	**14**	147	490	0.20×10^{-3}
$(c)CH_3CH=CHCH_3$	590-18-1	**15**	1340	1 310	8.32×10^{-8}
$(t)CH_3CH=CHCH_3$	624-64-6	**16**	434	847	3.51×10^{-8}
$(c)EtCH=CHEt$	7642-09-3	**17**	3563	3 250	1.78×10^{-7}
$(t)EtCH=CHEt$	13269-52-8	**18**	388	1 850	2.11×10^{-7}
$(c)EtCH=CHCH_3$	627-20-3	**19**	2690	2 100	
$(t)EtCH=CHCH_3$	646-04-8	**20**	568	1 330	
$(c)i$-$PrCH=CHCH_3$	691-38-3	**21**	2624	773	
$(t)i$-$PrCH=CHCH_3$	674-76-0	**22**	325	600	
$(c)t$-$BuCH=CHCH_3$	762-63-0	**23**	1029	650	
$(t)t$-$BuCH=CHCH_3$	690-08-4	**24**	162	79.5	
$(c)i$-$PrCH=CHEt$	15840-60-5	**25**	2769	742	
$(t)i$-$PrCH=CHEt$	692-24-0	**26**	245	555	
$(c)t$-$BuCH=CHEt$	690-92-6	**27**	1704	998	
$(t)t$-$BuCH=CHEt$	690-93-7	**28**	121	108	
$(CH_3)_2C=CHCH_3$	513-35-9	**29**	3030	66 700	2.15×10^{-4}
(Z)-$Et(CH_3)C=CHCH_3$	922-62-3	**30**	4835[e]	79 200	
(E)-$Et(CH_3)C=CHCH_3$	616-12-6	**31**	2284[e]	75 700	
t-$BuCH=C(CH_3)_2$	107-40-4	**32**	1462[e]	13 720	
$(CH_3)_2C=C(CH_3)_2$	563-79-1	**33**	7760	91 700	3.42×10^{-4}
$C_6H_5CH=CH_2$	100-42-5	**34**	62	84.8	0.240×10^{-6}
$C_6H_5(CH_3)C=CH_2$	98-83-9	**35**	265	113	0.133×10^{-3}
$(t)C_6H_5CH=CHCH_3$	873-66-5	**36**	118	170	1.12×10^{-7}
$(t)C_6H_5CH=CHC_6H_5$	103-30-0	**37**	8.05	0.545	0.71×10^{-10}
$(C_6H_5)_2C=CH_2$	530-48-3	**38**	20.1	1 670	
$(c)PrCH=CH_2$	693-86-7	**39**	410[h]	$>10^6$[g]	0.254×10^{-3}
Cyclohexene	110-83-8	**40**	786[h]	11 400[i]	0.443×10^{-7}

[a] Values were obtained from ref 4a and 4b unless otherwise noted. [b] Values were obtained from ref 4c unless otherwise noted. Units changed to s^{-1}. The rate constant k_g is a global rate constant and is equal to $k_{Br_2} + Kk_{Br_3} - [Br]/(1 + K[Br^-])$. [c] Values were obtained from ref 3a–d unless otherwise noted. [d] As discussed in ref 3b, this rate is artificially low due to the method of extrapolation. However, ethylene is at least 10^4 times less reactive than propene. [e] C. L. Dean, D. G. Garratt, and G. H. Schmid, unpublished data. [f] Calculated from $k_g(1 + K[Br^-]) = k_{Br_2} + Kk_{Br_3} - [Br^-]$, E. Bienvenue-Goetz and J. E. Dubois, *J. Org. Chem.*, **40,** 221 (1975). [g] D. G. Garratt, A. Modro, K. Oyama, G. H. Schmid, T. T. Tidwell, and K. Yates, *J. Am. Chem. Soc.*, **96,** 5295 (1974). [h] Reference 11. [i] J. E. Dubois and P. Fresnet, *Tetrahedron Lett.*, 2195 (1974). [j] Registry no.: 933-01-7.

In Figure 2, log k_2^{ArSCl} is plotted against log $k_g^{Br_2}$. Here a reasonable straight line is obtained. Three compounds, cyclopropylethylene (**39**), 1,1-diphenylethylene (**38**), and 1,1-di-*tert*-butylethylene (**11**), lie far off the line and the latter is off the figure. The latter two compounds are subject to severe steric problems which appear to be especially acute in the addition of 4-chlorobenzenesulfenyl chloride to **11**. The remaining data can be correlated by eq 1 where $r = 0.849$. The dashed line represents this equation in Figure 2. A better correlation, eq 2, can be obtained by omitting compounds **15, 17, 19, 21, 23, 35,** and **27,** all cis alkenes. The solid line in Figure 2 represents this equation where $r = 0.935$.

$$\log k_2^{ArSCl} = 0.412 \log k_g^{Br_2} + 1.52 \quad (1)$$

$$\log k_2^{ArSCl} = 0.392 \log k_g^{Br_2} + 1.44 \quad (2)$$

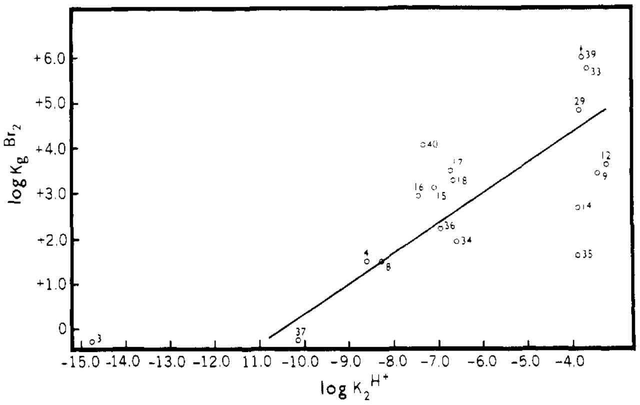


Figure 1. Plot of log $k_2^{H^+}$ vs. log $k_g^{Br_2}$. The least-square line for all points except no. 39 is log $k_2^{H^+} = 1.50 \log k_g^{Br_2} - 10.50$; $r = 0.789$.

However, the object of such plots is not to obtain the best correlation by eliminating part of the data but rather to discern trends in the structure–reactivity profile of *all the available data.* Indeed, it is the compounds that do not fit such correlations that are often the most interesting and mechanistically informative. Using this approach, the data are quite informative as to the significant influences on the reactivity.

The general trend of the data in Figure 2 establishes the similarity in the structure–reactivity profiles of the additions

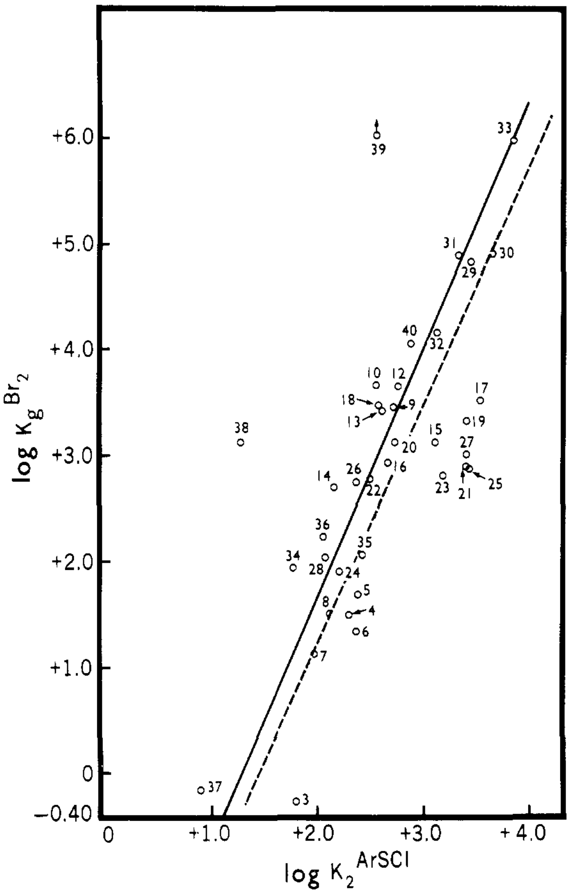


Figure 2. Plot of log k_2^{ArSCl} vs. $k_g^{Br_2}$. The dashed line represents eq 1 while the solid line represents eq 2.

of bromine and arenesulfenyl chloride. This is in accord with a general mechanism involving a bridged rate-determining transition state for both reactions. The effect of substituents is greater on the rate of bromination than on the rate of sulfenyl chloride addition. This has been previously noted for a more limited set of compounds.[4a]

Deviations from the correlation by compounds, such as cyclopropylethylene, 1,1-diphenylethylene, and 1,1-di-*tert*-butylethylene, suggest that either they react by a different mechanism or unusual steric or polar factors are present in their rate-determining transition states.

The high rate of bromination of cyclopropylethylene may be explained by a mechanism involving an open-ion-like rate-determining transition state. Consistent with this view is the formation of ring-opened products.[9] This change in mechanism is due to the great ability of a cyclopropyl group to stabilize an adjacent carbonium ion by resonance electron donation.[10] Enhancing this effect is the inability of the cyclopropyl ring to stabilize a bridged ion, since its inductive effect is electron withdrawing. Bromination of 1-cyclopropylpropene and 1,1-dicyclopropylethylene is also too fast to measure.[11]

For 1,1-diphenylethylene, the deviation results from either an enhanced bromination rate or a decreased rate of sulfenyl chloride addition. The mechanism has been proposed to involve an open-ion-like rate-determining transition state[12] in bromination which would account for its deviation. However, steric retardation cannot be ruled out. Severe steric hindrance between the *tert*-butyl groups and the electrophile (either bromine or arenesulfenyl chloride), resulting in an abnormally slow rate of addition, appear likely to be responsible for the deviation of 1,1-di-*tert*-butylethylene from the correlation.[13,14]

Correlations such as those in Figure 2 define "normal" structure–reactivity behavior and enable us to recognize "abnormal" behavior. For example, it has been known for many years that the ratio $k_{cis}/k_{trans} > 1$ for the addition of bromine and arenesulfenyl chlorides to aliphatic isomeric alkenes. However, it is never been possible to establish whether addition to the cis or trans series is abnormal. From Figure 2, it appears that the cis series deviates from the main body of data. This deviation is not due to a change in the mechanism, since all evidence is in accord with a mechanism involving a bridged rate-determining transition state for addition to all these alkenes. The deviations arises from either an abnormal rate of sulfenyl chloride addition or a diminished rate of bromination of the cis alkenes. It does not appear that the bromination rates would be retarded and instead it appears that addition of sulfenyl chloride is favored.

Another example of the mechanistic value of Figure 2 is the case of additions to styrene (**34**), 2-phenylpropene (**35**), *trans*-1-phenylpropene (**36**), and stilbene (**37**). It has been claimed that the rate-determining transition state for bromination of these compounds resembles an open 2-bromocarbonium ion.[12] If this were the case, serious deviations would be expected as in the case of 1,1-diphenylethylene. The fact that the phenyl-substituted alkenes correlate well with the aliphatic alkenes is strong evidence for a bridged rate-determining transition state. The products which are formed by nonstereospecific addition must result from an open ion formed after the rate-determining step.

The preceding examples illustrate the utility of this method. Correlations such as those in Figures 1 and 2 are based upon the assumption that the mechanisms of the model reactions do not change with changes in alkene structure. This assumption is justified by the results of extensive studies on hydration and arenesulfenyl chloride additions of alkenes. So far no exceptions to their general mechanisms have been found.

Thus, the use of the structure–reactivity profiles of these two model reactions provides a valuable method of obtaining information of the structure of the rate-determining transition state. It can be used to test other reactions such as oxymercuration[16] and thallation in which there is some controversy regarding their rate-determining transition-state structure.

Acknowledgment. Continued financial support by the National Research Council of Canada is gratefully acknowledged.

References and Notes

(1) Part 17, Reactions of Sulfenyl Halides and their Derivatives. For Part 16, see G. H. Schmid, A. Modro, D. G. Garratt, and K. Yates, *Can. J. Chem.*, **54**, 3045 (1976).

(2) P. R. Wells, "Linear Free Energy Relationships" Academic Press, New York, N.Y., 1968.

(3) (a) K. Oyama and T. T. Tidwell, *J. Am. Chem. Soc.*, **98**, 947 (1976). (b) W. K. Chwang, V. J. Nowlan, and T. T. Tidwell, *J. Am. Chem. Soc.*, **99**, 7233 (1977). (c) V. J. Nowlan and T. T. Tidwell, *Acc. Chem. Res.*, **10**, 252 (1977). (d) G. H. Schmid and V. J. Nowlan, *Can. J. Chem.*, **54**, 695 (1976). (e) A. F. Hegarty, J. S. Lomas, V. W. Wright, E. D. Bergmann, and J. E. Dubois, *J. Org. Chem.*, **37**, 2222 (1972). (f) J. H. Rolston and K. Yates, *J. Am. Chem. Soc.*, **91**, 1483 (1969).

(4) (a) G. H. Schmid and D. G. Garratt, *Can. J. Chem.*, **51**, 2463 (1973). (b) G. H. Schmid, C. L. Dean, and D. G. Garratt, *Can. J. Chem.*, **54**, 1253 (1976). (c) G. Mouvier and J. E. Dubois, *Bull. Soc. Chim. Fr.*, **72**, 1441 (1969). (d) M. Charton and B. I. Charton, *J. Org. Chem.*, **38**, 1631 (1973).

(5) R. Fellows and R. Luft, *J. Am. Chem. Soc.*, **95**, 5593 (1973).

(6) H. J. Bergmann, G. Collin, G. Just, G. Müller-Hagen, and W. Pritzkow, *J. Prakt. Chem.*, **314**, 285 (1972).

(7) For reviews of electrophilic addition reactions, see: (a) G. H. Schmid and D. G. Garratt, in "Chemistry of Double Bonded Functional Groups," Supplement A, Part 2, S. Patai, Ed., Wiley London, 1977, Chapter 9. (b) F. Freeman, *Chem. Rev.*, **75**, 439 (1975). (c) R. Bolton, *Compr. Chem. Kinet.*, **9**, 1 (1973). (d) P. B. D. de la Mare, "Electrophilic Halogenation", Cambridge University Press, New York, N.Y., 1976.

(8) (a) J. R. Dubois, A. F. Hegarty, and E. D. Bergmann, *J. Org. Chem.*, **37**, 2218 (1972). (b) J. E. Dubois and X. Q. Huynh, *Bull. Soc. Chim. Fr.*, 1436 (1968).

(9) D. F. Shellhamer, D. B. McKee, and C. T. Leach, *J. Org. Chem.*, **41**, 1972

(1976).
(10) H. C. Brown and J. D. Cleveland, *J. Org. Chem.*, **41**, 1792 (1976).
(11) T. T. Tidwell, G. H. Schmid, V. M. Csizmadia, and T. R. Cerksus, *Can. J. Chem.*, in press.
(12) J. E. Dubois, A. F. Hegarty, and E. D. Bergmann, *J. Org. Chem.*, **37**, 2218 (1972).
(13) C. L. Dean, D. G. Garratt, T. T. Tidwell, and G. H. Schmid, *J. Am. Chem. Soc.*, **96**, 4958 (1974).
(14) (a) D. Grosjean, G. Mouvier, and J. E. Dubois, *J. Org. Chem.*, **41**, 3869 (1976). (b) D. Grosjean, G. Mouvier, and J. E. Dubois, *J. Org. Chem.*, **41**, 3872 (1976).
(15) M. F. Rausse and J. E. Dubois, *J. Org. Chem.*, **39**, 2441 (1974).
(16) I. C. Ambridge, S. K. Dwight, C. M. Rynard, and T. T. Tidwell, *Can. J. Chem.*, in press.

Onium Ions. 17.[1a] Improved Preparation, Carbon-13 Nuclear Magnetic Resonance Structural Study, and Nucleophilic Nitrolysis (Nitrative Cleavage) of Diarylhalonium Ions

George A. Olah,* Toru Sakakibara,[1b] and Gregorio Asensio[1b]

Institute of Hydrocarbon Chemistry, Department of Chemistry, University of Southern California, Los Angeles, California 90007, and Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received July 5, 1977

An improved method of preparation of diarylchloronium and diarylbromium ions is described from their corresponding arenediazonium ions by decomposition in haloarenes in the presence of trifluoro- (trichloro-) acetic acid or 2,2,2-trifluoroethyl alcohol. ^{13}C NMR spectroscopic study of the prepared halonium ions shows that nearly equal amounts of charge are transmitted into the two aryl rings regardless of the methyl substitution in one or both rings, suggesting that canonical structures such as I–III are only limited resonance contributors. The potential utility of symmetrical and unsymmetrical diarylchloronium, -bromonium, and -iodonium ions in their nucleophilic nitrolysis with sodium nitrite, giving nitroarenes, was studied. The relative reactivity of the 4-tolyl, phenyl, 3-tolyl, and 2-tolyl salts has been established as 1.0, 3.0, 3.6, and 14.1, respectively. Substitution of tetraphenylborate for hexafluorophosphate as counterion did not affect the product distribution in the nitration reaction. The data reported are best accommodated by an S_N2-like mechanism controlling the collapse of ionic diarylchloronium nitrites, initially formed by displacement of the corresponding counterion, to give nitro- and chlorobenzene derivatives.

Whereas diaryliodonium ions have been extensively studied,[2] only limited data are available on diarylchloronium and -bromonium ions[2] in spite of the high potential utility of these ions as electrophilic arylating agents.[3] This can be attributed to the extremely low yields (0.6–6.6%) obtained in their preparation by Nesmeyanov and co-workers using the decomposition of aryldiazonium tetrafluoroborates in chloro- or bromoarenes.[4–7] Recently Nesmeyanov and co-workers reported an improved preparation of diarylbromium ions by reacting aryllithiums with BrF_3 in 9–28% yields.[8] This method is limited to the preparation of symmetrical diarylbromonium ions. Further difficulties involved in handling BrF_3 and its explosive nature with phenyllithium make the method of little use.

The preparative utility of diarylbrominium tetrafluoroborates was demonstrated by McEwen and Lubinknowski[9a] in their nucleophilic displacement reaction with sodium alkoxides, giving exclusively phenyl alkyl ethers. The corresponding diaryliodonium salts gave under the same conditions, however, aromatic hydrocarbons as the major products[9b] (via a radical path). Reutov and co-workers[9c] carried out the reaction between diarylhalonium salts and triphenylphosphine in light to give (via a radical path) tetraphenylphosphonium ions in 82–92% yields. Nesmeyanov and his co-workers[9d] briefly reported that diarylbromonium and -chloronium ions are quite reactive toward many common nucleophiles, including amines, sodium nitrate, sodium azide, and sodium cyanide. Diphenyliodinium tetrafluoroborate treated with sodium nitrite in aqueous dioxane gave nitrobenzene in 70% yield.[9a] A similar reaction with phenyl-*p*-tolyliodonium tetrafluoroborate yielded a mixture of nitrobenzene and *p*-nitrotoluene in a ratio of 2.5:1.[9d]

A systematic study of the reactivity of diarylchloronium and -brominium ions with nucleophiles, however, has not yet been reported since these halonium salts have been obtained previously only in extremely low yields and were believed to be quite unstable compounds.[10]

Interested in the chemistry of organic halonium ions, we now wish to report an improved method of preparation of diarylchloronium and diarylbrominium ions from their corresponding arenediazonium ions by decomposition in haloarenes in the presence of trifluoro- (trichloro-) acetic acid or 2,2,2-trifluoroethyl alcohol. The developed, improved general method for the preparation of these halonium ions also allowed a systematic study of the nucleophilic nitration of a series of methyl-substituted diarylhalonium salts with sodium nitrite.

Results and Discussion

Preparation of Diarylchloronium and Diarylbromonium Ions. When phenyldiazonium hexafluorophosphate was heated at 60–65 °C in chlorobenzene in the presence of trifluoroacetic acid for 2 h, the reaction mixture subsequently extracted with water, and the aqueous solution neutralized with sodium hydrogen carbonate, the addition of sodium tetraphenylborate caused precipitation of the diphenylchloronium tetraphenylborate salt. The yield of the purified salt recrystallized from acetone–ether was 13%. GC and IR analysis of the organic layer indicated the presence of fluorobenzene (36%), formed in the competitive Schiemenn reaction, and phenyl trifluoroacetate. In addition to trifluoroacetic acid, 2,2,2-trifluoroethyl alcohol, acetic acid, and trichloroacetic acid were also found to be effective; they give the diphenylchloronium salt in 9.0, 4.0, and 8.0% yields, along with fluorobenzene in 40, 51, and 33% yields, respectively. Phenyl 2,2,2-trifluoroethyl ether, phenyl acetate, and phenyl trichloroacetate were formed (based on IR and/or NMR spectroscopy) as the byproducts. Similar arylation failed to take

---

* Address correspondence to University of Southern California.