Electrophilic Bromination of Fluoro Olefins: Syn vs. Anti Addition[1]

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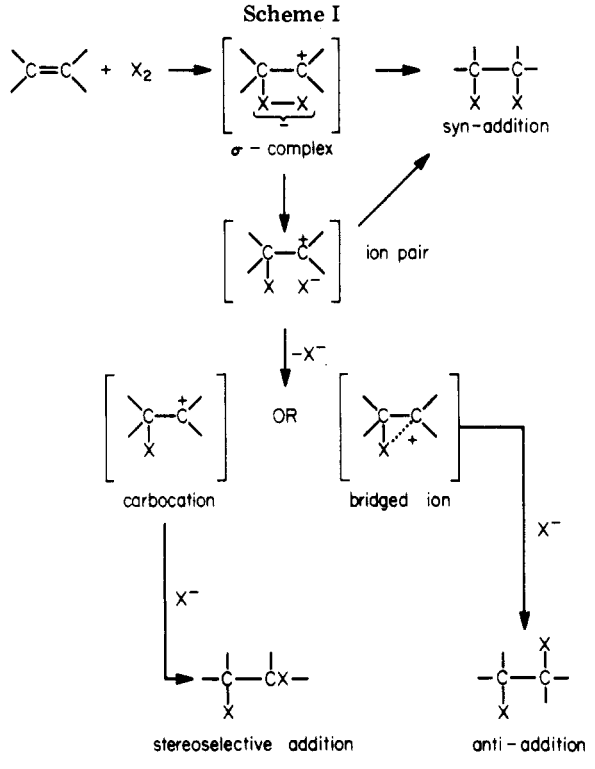
The ionic addition of bromine in glacial acetic acid to 4-$RC_6H_4CF{=}CFX$ (R = CO_2H, Br, H, CH_3, OCH_3; X = Cl, CF_3) and 4-$RC_6H_4CH{=}CFCl$ (R = Br, CH_3) has been studied. For all olefins the 1,2-dibromo adduct is the predominant product, with a minor amount of the 1-acetoxy-2-bromo adduct being formed. For R = CH_3 and OCH_3 the stereochemistry of the 1,2-dibromo adduct results from preferential suprafacial addition of bromine to the double bond. This is explained by a σ complex or ion pair (with no bromine bridging) that collapses to the suprafacial adduct before ion separation, bromine bridging, or bond rotation can occur. The amount of suprafacial addition decreases as the bromine concentration is increased, for R = OCH_3 (when compared with R = CH_3) and for replacement of the vinyl fluorine on the α-carbon with a hydrogen. The olefins with R = CO_2H, Br, and H preferentially form the dibromo adducts in an antarafacial process for X = Cl; for X = CF_3 the addition exhibits a slight stereoselective preference for the erythro diastereomer.

The kinetics and the stereochemistry of the ionic bromination of acyclic olefins have been extensively studied in recent years. The goal of these investigations has been a precise description of the structures of the intermediates and transition states involved in the reaction. It has been found that the rate-determining transition state is a function of both alkene structure and solvent. For simple acyclic alkyl olefins a bridged transition state leading to a bromonium ion is involved.[2-6] The result is that the stereochemistry of the addition is almost exclusively anti (antarafacial addition).

For aromatic olefins the structure of the rate-determining transition state and intermediate are variable. Yates and co-workers have performed kinetic studies and concluded that while the rate-determining transition state has at least partial bridging character, the subsequent intermediate can be either a bridged or an open cation.[4,7-9] Dubois has investigated the bromination of substituted stilbenes and demonstrated that the nature of the aromatic substituent (whether it is electron donating or withdrawing) controls the structure of the intermediate cation.[10-12]

The effect of substituents and solvent on the stereochemistry of the reaction has been studied. For instance, *cis*- and *trans*-1-phenylpropenes, $C_6H_5CH{=}CHCH_3$, form dibromo adducts with greater than 74% anti addition in acetic acid, carbon tetrachloride, chloroform, or methylene chloride.[3,13] *trans*-1-Phenylpropene shows a marked substituent effect in the stereochemistry of dibromide formation. The reaction is nonstereoselective for the 4-methoxy derivative (indicative of a benzylic cation intermediate) and antistereospecific for the 3,5-bis(trifluoromethyl) derivative, a brominum ion intermediate.[13,14] Finally, the amount of bridging by bromine is influenced by the solvent: as the polarity of the solvent increases the antistereospecificity decreases.[7,11,15,16]

Scheme I



While a mechanism involving a bridged intermediate adequately accounts for the stereochemistry of bromination reactions, it cannot be merely extrapolated to the addition reactions of fluorine and chlorine. These halogens react with certain acyclic olefins and form dihalides where syn addition predominates (suprafacial addition).[17] A reaction path for electrophilic halogenation that accounts for both syn and anti addition products has been proposed by de la Mare (Scheme I).[15] In this mechanism, the collapse of the first intermediate, the σ complex, leads to syn addition. The σ complex can also lose the nucleophile, X^-, and form an ion pair which still gives rise to preferential syn addition. Separation of the ion pair leads to a carbocation or bridged ion, depending upon the halogen. The carbocation would lead to nonstereospecific dihalides

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(17) For discussions of syn additions see ref 15 pp 55-8 and 75-9 and the following: Chambers, R. D.; James, S. R. In "Comprehensive Organic Chemistry"; Barton, D., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 1, Part 3, p 507. Specific references are: (a) Merritt, R. F. *J. Am. Chem. Soc.* **1967**, *89*, 609. (b) Fahey, R. C.; Schubert, C. *Ibid.* **1965**, *87*, 5172. (c) Gambaretto, G.; Napoli, M. *Atti Ist. Veneto Sci., Lett. Arti, Cl. Sci. Mat. Nat.* **1969**, *127*, 393; *Chem. Abstr.* **1971**, *74*, 3137.

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Table I. Ionic Bromination Reactions[a]

$$4\text{-}RC_6H_4CF{=}CFX + Br_2 \xrightarrow[\text{dark}]{HOAc} \text{products}$$

compd	X	R	isomer	reactant concn, M[b]	1,2-Br_2 adduct % yield[c]	1,2-Br_2 adduct erythro/threo[c]	1,2-Br_2 adduct syn/anti	1-OAc-2-Br adduct, % yield[c]	isomerized olefin, % yield[c]	reacn time, days
1a	Cl	CO_2H	*E*	1	90	28:72[d]	1:2.6	10		4
			Z	1	80	86:14[d]	1:6.1	12		4
1b	Cl	Br	*E*	1	42	24:76	1:3.2	3	8	18
			E	10^{-2}	10	*e*			36	38
			Z	1	87	78:22	1:3.5	5		18
			Z	10^{-2}	12	56:44	1:1.3		6	39
1c	Cl	H	*E*	1	55	34:66	1:1.9	10	5	6
			Z	1	60	79:21	1:3.8	7		5
1d	Cl	CH_3	*E*	1	41	42:58	1:1.4	5		3
			E	10^{-2}	48	75:25	3.0:1	14		4
			Z	1	95	55:45	1:1.2	5		3
			Z	10^{-2}	39	28:72	2.6:1	11		7
1e	Cl	OCH_3	*E*	1	33	49:51	1:1	<3		1
			E	10^{-2}	35	59:41	1.4:1		8	3
			Z	1	95	51:49	1:1			1
			Z	10^{-2}	51	41:59	1.4:1			3
2a	CF_3	CO_2H	*E*	1	47	59:41[d]		5		4
			Z	1	27	55:45[d]		<3		3
2b	CF_3	Br	*E*	1	76	60:40		8		8
			E	10^{-2}	3	*e*				38
			Z	1	36	67:33		5		8
			Z	10^{-2}	<2	*e*				38
2c	CF_3	H	*E*	1	86	53:47		7		13
			E	10^{-2}	7	*e*				13
			Z	1	81	63:35		7		13
2d	CF_3	CH_3	*E*	1	90	32:68	2.1:1	3	3	3
			E	10^{-2}	47	10:90	9.0:1	<2		4
			Z	1	79	86:14	6.1:1	5		15
			Z	10^{-2}	21	86:14	6.1:1	8	29	38
2e	CF_3	OCH_3	*E*	1	100	45:55				3
			E	10^{-2}	61	21:79	3.8:1	<2		3
			Z	1	94	45:55				3
			Z	10^{-2}	56	81:19	4.3:1		20	3

[a] All reactions were performed in the dark at room temperature. [b] The initial concentration of olefin and bromine was either ca. 1.4 M each or ca. 3×10^{-2} M each. [c] Determined by ^{19}F NMR. Ratios are ±3%. [d] Data from ref 22. [e] The erythro/threo ratio could not be accurately determined.

while the bridged ion would give rise to predominant anti addition.

For fluorine and chlorine, large amounts of syn addition products are formed from certain olefins due to the presence of the σ complex. For the ionic addition of bromine, syn addition has not been observed routinely. This is attributed to the tendency of the bromine complexes to lose tribromide ion and to form a bridged ion.[15,18]

This paper reports the first examples where both cis and trans acyclic olefins undergo preferential syn addition of bromine, indicating the intervention of the bromine σ complex in the reaction mechanism. To be sure, there are reports of syn addition of bromine to acyclic olefins, but these are not true instances of syn addition; rather, they are stereoselective additions arising from bond rotation in the intermediate cation. For example, *cis*-1-phenylpropene reacts with bromine in dioxane to give 80% of the syn adduct. However, the trans isomer gives 71% of the anti adduct. This similarity in product ratios was interpreted as solvation of the carbocation intermediate by dioxane which reduces the amount of bromine bridging and allows rotation about the C_α–C_β bond.[7] The bromination of *cis*-stilbene leads to preferential syn addition in certain solvents, while *trans*-stilbene gives the trans adducts in the same solvents.[19] Again, this can be interpreted as a result of rotational freedom in the intermediate carbocation. Finally, the addition to diethyl maleate and diethyl fumarate is stereoselective, with the *meso*-dibromide being formed in each case.[20]

Results

The fluorinated olefins in this study were a series of phenyl-substituted ethylenes and propenes. The 1-aryl-2-chloro-*F*-ethylenes (**1**) and 1-aryl-*F*-propenes (**2**) were

$4\text{-}RC_6H_4CF{=}CFX$ $\quad$ $4\text{-}RC_6H_4CH{=}CFCl$

1, X = Cl $\quad$ **3**

2, X = CF_3

a, R = CO_2H; **b**, R = Br; **c**, R = H; **d**, R = CH_3; **e**, R = OCH_3

prepared via the reaction of the organolithium compound with chloro-*F*-ethylene or *F*-propene.[21,22] The carboxy-substituted olefins were prepared via carbonation of the Grignard reagent.[22,23] The 2-chloro-2-fluorostyrenes **3** were prepared from the aldehydes via a Wittig reaction.[24] The cis and trans isomers of all olefins were separated by preparative gas chromatography, and the isomeric purity

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of the separated isomers was verified by analytical gas chromatography and by ^{19}F NMR.

The distribution of products formed during the ionic reaction with bromine in glacial acetic acid with the *E* and *Z* isomers of **1** and **2** is listed in Table I. The predominant product in this reaction is the 1,2-dibromo adduct. The solvent-incorporated product, the 1-acetoxy-2-bromo adduct, is formed in minor amounts. Some isomerization of the starting olefin occurs and is most prevalant for the isomerization of the isomer with cis vinyl fluorines to the trans isomer (e.g., (*E*)-**1b** to (*Z*)-**1b**). The reaction times are variable and do not represent the time for optimum yield.

Due to the large differences in reactivity of the olefins, it is necessary to employ two reaction conditions in order to obtain reasonable rates of reaction. The olefins with R = CH_3 and R = OCH_3 react at ca. 10^{-2} M bromine concentrations. The olefins with the deactivating substituents react very slowly at this concentration, and it is necessary to use higher concentrations of bromine (ca. 1 M) to get a convenient rate of reaction.

As is the case with most fluorinated olefins, these olefins are very susceptible toward radical addition of bromine.[25] To minimize the radical reaction, the ionic reactions were performed in light-tight containers. At the end of the reaction time trimethylethylene was added to the reaction solution to scavenge any unreacted bromine before the solution was exposed to light.

The feature aspect of Table I is the stereochemistry of the 1,2-dibromo adducts. For **1a**, **1b**, and **1c** preferential anti addition (antarafacial addition) of bromine occurs. For **2a**, **2b**, and **2c** the formation of the erythro diastereomer is slightly favored, independent of the starting isomer. For olefins **1d**, **1e**, **2d**, and **2e** (R = CH_3, OCH_3) preferential syn addition (suprafacial addition) of bromine is observed at ca. 10^{-2} M bromine concentration. At ca. 1 M bromine concentration a substantial decrease and in some instances an inversion of the stereochemistry of the 1,2-dibromo adduct is seen.

The stereochemistry of the 1-acetoxy-2-bromo adducts formed during the reaction was not independently determined. However, for the adducts from **1** the formation appears stereospecific, as the *E* isomers always formed one diastereomer (*R,S*) while the *Z* isomers led to the other diastereomer (*R,R*). Formation of the acetoxy adduct from **2** appears to be stereoselective, as only one diastereomer can be detected regardless of the initial structure of the olefin. Authentic samples of the acetoxy compounds were prepared from **1d** and **2d** by reaction with Br_2 and $Hg(OAc)_2$[26] (eq 1). In these preparations both diastereomers are formed in approximately equal amounts.

$$\underset{\substack{\mathbf{1d},\ X = Cl\\ \mathbf{2d},\ X = CF_3}}{4\text{-}CH_3C_6H_4CF{=}CFX} \xrightarrow[\text{HOAc, dark}]{Br_2,\ Hg(OAc)_2} 4\text{-}CH_3C_6H_4C(OAc)FCFBrX \quad (1)$$

(25) Polyfluorinated olefins are usually reacted with bromine under radical conditions with the result that the number of additions that are known to be ionic are limited. Details on the effect of substituents on reaction mechanism and stereochemistry, until recently, have been lacking. For example, see: (a) Chambers, R. D.; Mobbs, R. H. *Adv. Fluorine Chem.* **1965**, *4*, 78–81. (b) Dyatkin, B. L.; Mochalina, E. P.; Knunyants, I. L. *Fluorine Chem. Rev.* **1969**, *3*, 45–72. (c) Chambers, R. D. "Fluorine in Organic Chemistry"; Wiley: New York, 1973; pp 142–73. (d) Banks, R. E. "Fluorocarbons and Their Derivatives", 2nd ed.; MacDonald: London, 1970; pp 36–9. (e) Lovelace, A. M.; Rausch, D. A.; Postelnek, W. *ACS Monogr.* **1958**, *No. 138*, 33–4. (f) Hudlicky, M. "Chemistry of Organic Fluorine Compounds", 2nd ed.; Halsted: New York, 1976; pp 214–6.

(26) Knunyants, I. L.; Pervova, E. Y.; Tyuleneva, V. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1956**, 843.

Table II. Ionic Bromination Reactions: 1,2-Dibromo Adduct Product Ratios[a]

$$4\text{-}RC_6H_4CH{=}CFCl + Br_2 \xrightarrow[\text{dark}]{HOAc} 4\text{-}RC_6H_4CBrHCBrFCl$$

compd	R	isomer	*R,S*/*R,R*[b]	syn/anti
3b	Br	*E*	73:27	1:2.7
		Z	29:71	1:2.4
3d	CH_3	*E*	42:58	1.4:1
		Z	61:39	1.6:1

[a] All reactions were performed in the dark at room temperature. The initial concentrations of reactants were ca. 1.4 M when R = Br and ca. 3×10^{-2} M when R = CH_3. [b] Diastereomer ratio determined by ^{19}F NMR, ±3%.

Table II lists the results of the ionic bromination of **3**. For the electron-withdrawing R = Br substituent preferential anti addition is observed while for R = CH_3 syn addition predominates.

The stereochemical structure assignments of the 1,2-dibromo adducts from **1**, **2**, and **3** are based on previous determinations[22] and on the stereospecific E2 elimination of bromine from the dibromo adduct by NaI.[22,27] The erythro/threo assignment to the dibromo adduct from **2d** was also confirmed when E2 debromination of a 32:68 erythro/threo mixture of the dibromo adduct yielded a 31:69 *E*/*Z* isomer mixture of **2d** (eq 2).

$$\underset{\text{32:68 erythro/threo}}{4\text{-}CH_3C_6H_4CFBrCFBrCF_3} \xrightarrow[\text{acetone}]{NaI} \underset{\text{31:69 } E/Z}{\mathbf{2d}} \quad (2)$$

The dibromo adducts from **3** were assigned stereochemical structures by first assuming that the *E* and *Z* isomers of **3b** underwent preferential anti addition of bromine. This established the relative configuration of the two diastereomers. This assignment was confirmed by the E2 debromination of a 66:34 *R,S*/*R,R* mixture of the dibromo adduct from **3d** which yielded a 67:33 *E*/*Z* isomer mixture of **3d** (eq 3).

$$\underset{\text{66:34 } R,S/R,R}{4\text{-}CH_3C_6H_4CHBrCFClBr} \xrightarrow[\text{acetone}]{NaI} \underset{\text{67:33 } E/Z}{\mathbf{3d}} \quad (3)$$

Finally, the reactions of (*E*)-**1d** and (*E*)-**2d** with bromine in methanol fail to yield any dibromo adduct (eq 4). The only product formed in either reaction is identified by ^1H and ^{19}F NMR and by mass spectroscopy as a 1-methoxy-2-bromo adduct, and in each instance only one diastereomer can be detected by ^{19}F NMR.

$$\underset{\substack{\mathbf{1d},\ X = Cl\\ \mathbf{2d},\ X = CF_3}}{(E)\text{-}4\text{-}CH_3C_6H_4CF{=}CFX} \xrightarrow[\text{MeOH, dark}]{Br_2} 4\text{-}CH_3C_6H_4C(OMe)FCFBrX \quad (4)$$

Discussion

The product distribution given in Table I for the ionic addition of bromine to **1** and **2** is roughly comparable to that reported by Rolston and Yates for the bromination of substituted styrenes in acetic acid.[3] They reported the major product to be the dibromide, with a 15–30% yield of the acetoxybromo adduct being formed. As Rolston and Yates detailed, these acetoxy bromides are also formed in a regiospecific manner, being 1-acetoxy-2-bromo adducts. This means there is considerable positive charge localized

(27) Mathai, I. M.; Schug, K.; Miller, S. I. *J. Org. Chem.* **1970**, *35*, 1733.

on the α-carbon and that this charge is not spread to the β-carbon via a strongly bridging bromine atom (i.e., a bromonium ion).

Dibromo Stereochemistry. The most interesting aspect of Table I is the stereochemistry of the 1,2-dibromo adducts and their mechanistic implications. For **2a**, **2b**, and **2c** the slight preference for the erythro diastereomer can be argued as being due to weak bridging by bromine. The bridging must be weak as the stereoselectivity of the reaction can arise only by rotation about the C_α–C_β bond. That some bridging must be present can be concluded from the stereochemistry of the radical addition of bromine to **2a**, **2b**, and **2d** (Table IV, supplementary material). In the radical addition the erythro diastereomer is favored only very slightly over the threo form (erythro/threo ratio of 52:48). This close similarity is due to there being only a slight difference in stability of the intermediates in the radical reaction. The ionic reaction, however, shows a clearer preference for the erythro form. This indicates that the intermediate cation leading to the erythro diastereomer is more favorable, and a logical source for this change in the relative stabilities of intermediates is partial bromine bridging, which leads to the second bromine being added anti to the first.

For **1a**, **1b**, and **1c** a clear preference for anti addition of bromine is seen. The percentage of the anti adduct is similar to that reported for other styrene derivatives[3,13,14] and is indicative of an intermediate cation with strong bridging by bromine.

The difference in bromine bridging in the reactions for **1** and **2** can be explained by the substituents on the β-carbon. In **1**, a β-chlorine is present, and it is able to stabilize a partial positive charge on the β-carbon formed as a result of bromine bridging. Thus, the β-chlorine encourages bromine bridging. For **2**, the substituent is a β-trifluoromethyl which is incapable of stabilizing a positive charge. The result is that bromine bridging is less favorable, and bond rotation can now occur more easily.

The reactions of **1a**, **1b**, **1c**, **2a**, **2b**, and **2c** can be anticipated and explained by using examples from the literature. However, the ionic reactions of **1d**, **1e**, **2d**, and **2e** at 10^{-2} M bromine concentration are unique as they show 59–90% syn addition of bromine. This preference for suprafacial addition cannot involve an intermediate that has even weak partial bromine bridging as this would lead either to anti addition or to a stereoselective process. Other work has shown that dibromides are formed in acetic acid only from intimate ion pairs,[7] so the intervention of solvent-separated benzylic cation–bromide ion intermediates can be eliminated. This intermediate would lead to random stereochemistry and should result in an increase in the amount of solvent-incorporated product, which was not seen.

Therefore, the more reasonable intermediate for the reaction is the σ complex or ion pair shown in Scheme I.[28] This mechanism not only accounts for the stereochemistry of the reaction but also is in agreement with other observations. It is known that the rate of bromination of styrene has first- and second-order dependence on bromine concentration. At bromine concentrations of 10^{-2}–10^{-3} M in alcoholic solvents the overall process is substantially first order in bromine. In less polar solvents (e.g., acetic acid) or at higher bromine concentrations the second-order process becomes dominant.[18,31-33] Evidently, the second molecule of bromine helps to polarize the first in the transition state leading to the bridged ion. It has also been noted that the ease of tribromide ion formation should be a strong driving force for the conversion of the σ complex (or ion pair) into the bridged ion (Scheme I).[15] An increase in bromine concentration would lead to a greater proportion of the dibromide resulting from a solvent-separated benzylic cation or bridged ion. This would lower the amount of syn addition and may even cause anti addition to become the preferred reaction. This is seen to occur as the brominations for **1d**, **1e**, **2d**, and **2e** are compared at 10^{-2} and 1 M bromine concentrations.

For **1d** the 100-fold increase in bromine concentration causes a change from syn addition to a slight preference for anti addition. For **1e** the higher concentration leads to equal formation of the erythro and threo diastereomers. These reactions can be interpreted as a competition between the collapse of the σ complex (or ion pair) to form the *syn*-dibromide adduct and the conversion of the σ complex by bromine (with loss of tribromide) to a bridged ion. The same trend is seen for **2d** and **2e** where an increase in bromine concentration causes a decrease in the amount of syn addition. The only exception is the *Z* isomer of **2d** which can be explained by its very slow rate of reaction with bromine. The rate-determining step is formation of the σ complex which immediately collapses to the syn adduct before further reaction with bromine can occur.

The preference for syn addition of bromine must be critically related to the substituents on the α-carbon. This can be argued qualitatively from several points. It is known that an α-methyl[3] or an α-chloro[34] substituent in a styrene derivative decreases the amount of bromine bridging in an intermediate cation. The same can be expected for an α-fluorine, which serves to stabilize the charge at the α-carbon and reduce the degree of delocalization into the benzene ring. It follows that the greater the charge density at the α-carbon, the greater the driving force for collapse of the σ complex to give the syn adduct. This can be seen in the reactions of **3b** and **3d** where an α-hydrogen is present. The *E* and *Z* isomers of **1b** and **3b** give comparable amounts (within the error limits of the experiment—note that (*E*)-**1b** and (*Z*)-**3b** have the same relative configurations) of the anti adducts. However, **3d** gives substantially less of the syn adduct than **1d** does. This is due to the α-hydrogen in **3d** not being able to stabilize a positive charge at the α-carbon and greater delocalization into the ring occurs. The driving force for collapse of the complex to the syn adduct is decreased, and the intermediate has more time to undergo rotation about the C_α–C_β bond or to lose bromide and form a bridged ion. Either instance results in a decrease in syn stereospecificity.

A similar dependence on charge density at the α-carbon can be seen by comparison of **1d** and **2d** (R = CH_3) with **1e** and **2e** (R = OCH_3). The methoxy group is better able to stabilize the positive charge than the methyl group, greater delocalization into the ring occurs, and, as ration-

(28) It is possible for the ion pair in Scheme I to be formed directly without the intervention of the σ complex. However, bromine–olefin complexes are known,[29] although their role in the addition reaction is not understood.[29,30] Kinetic studies[18] have been interpreted as supporting their existence on the reaction coordinate for bromination.

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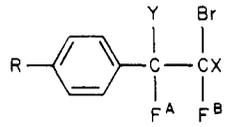
(33) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1483.

(34) Hamman, S.; Beguin, C. G. *J. Fluorine Chem.* **1979**, *13*, 163.

Table III. ^{19}F NMR Data of Diastereomers[a,b]



Y	X	R	isomer		$\phi^*_{F^B}$	$\phi^*_{CF_3}$	J_{F^A,F^B}	J_{F^A,CF_3}	J_{F^B,CF_3}
Br	Cl	Br	erythro	112.4	63.6		23.7		
			threo	111.1	62.6		22.8		
Br	Cl	CH_3	erythro	114.4	61.8		23.0		
			threo	113.0	60.6		23.3		
Br	Cl	OCH_3	erythro	111.5	63.3		23.4		
			threo	110.1	62.0		23.3		
Br	CF_3	Br	erythro	124.9	115.7	69.3	20.6	8.5	12.8
			threo	124.9	112.5	69.8	24.9	9.5	9.5
Br	CF_3	CH_3	erythro	125.7	115.9	70.7	21.2	8.1	12.8
			threo	125.7	112.9	71.3	24.6	9.5	9.5
Br	CF_3	OCH_3	erythro	125.6	115.1	70.9	21.9	8.5	13.0
			threo	125.6	112.4	71.5	24.9	9.6	9.6
O_2CCH_3	Cl	CO_2H	*R,S*	112.7	64.6		12.5		
			R,R	113.6	66.6		12.4		
O_2CCH_3	Cl	Br	*R,S*	113.8	70.3		13.6		
			R,R	112.8	70.8		12.4		
O_2CCH_3	Cl	H	*R,S*	119.2	73.7		12.6		
			R,R	118.2	74.2		12.4		
O_2CCH_3	Cl	CH_3	*R,S*	117.5	70.0		11.9		
			R,R	116.4	70.4		11.7		
O_2CCH_3	CF_3	CH_3	*R,S*	136.7	117.8	72.9	12.7	8.1	12.5
			R,R	135.8	118.3	72.7	9.9	8.1	9.8

[a] Chemical shifts are in parts per million upfield from external $CFCl_3$, ±0.3 ppm; coupling constants are in hertz, ±0.5 Hz. [b] Chemical shift assignments are based on 4-$HO_2CC_6H_4CFBrCFBrX$ (X = Cl, CF_3).[22]

alized above, this results in a decrease in the amount of syn addition for **1e** and **2e**.

The prominence of syn addition to **1d**, **2d**, and **3d** is in sharp contrast with the reaction of *trans*-anethole, 4-$CH_3OC_6H_4CH{=}CHCH_3$, where bromine addition leads to an erythro/threo ratio of 63:37 via a nonbridged intermediate cation.[13] As the reactions of **1e** and **2e** show a significant decrease in the amount of syn addition, it was concluded that the reactions of *cis*- and *trans*-4-$CH_3C_6H_4CH{=}CHCH_3$ would provide a better model for comparison with **1d**, **2d**, and **3d**. Reaction of the cis olefin in acetic acid in the dark leads to formation of the dibromo adduct with an erythro/threo ratio of 64:36. The trans olefin yields a ratio of 67:33. The reaction is stereoselective and is in sharp contrast with the reactions of **1d**, **2d**, and **3d** where a preference for syn addition is observed.

The preferential syn addition of bromine has been observed previously for the gas–solid bromination of (*Z*)-**2e** under ionic and radical reaction conditions.[22] Stereospecific syn addition of bromine has been reported for some bicyclic olefins. Partially fluorinated norbornenes add bromine only under radical conditions to form the *exo-cis*-dibromides.[35] The adducts of cyclopentadiene with maleic anhydride,[36] *F*-cyclopentene, and *F*-cyclobutene[37] also yield *exo-cis*-dibromides. In these examples the formation of the *exo-cis*-dibromides was attributed to steric effects and coulombic repulsion between *endo*-fluorine and bromine in the intermediate radical. These are examples of addition to cyclic olefins where steric constraints are present on the reaction stereochemistry. Such constraints do not exist in **1**, **2**, and **3**, and the formation of the syn adduct can not be attributed to them.

Finally, the importance of the isomerization of the olefin must be addressed. It appears that isomerization did not occur during the reaction but took place when the reaction was being worked up. This can be deduced from the stereochemistry of the reactions. Most of the isomerizations involved conversion of olefins with cis vinyl fluorines to the trans isomers. In this study and in others[13] the trans isomers are the more reactive, and if the trans isomer was produced during the reaction, it would react faster with bromine than the cis isomer; this would cause a decrease in the syn/anti ratio, which was not seen. In addition, if isomerization did occur during the reaction, the trans isomer should have been consumed. This obviously did not happen, and it is only logical that appreciable isomerization did not occur *during* the reaction.

Acetoxy–Bromide Stereochemistry. The stereochemistry of the 1-acetoxy-2-bromo adducts from **1** mirrors that of the acetoxy halides formed from bromination and chlorination of *cis*- and *trans*-β-methylstyrene where the solvent attacked the intermediate cation predominantly from the anti side.[3,17b] This was explained by the bulk of the first-attached halogen atom precluding syn attack and by the fact that a solvent molecule would always be in a favorable position to attack from the anti side.

In the present study it was observed that the *E* isomers of **1** always gave rise to the same diastereomer of the 1-acetoxy-2-bromo adduct while the *Z* isomers of **1** led to formation of the other diastereomer. The dibromides from **1** are formed by preferential anti addition of bromine as are the dibromides from β-methylstyrenes.[3] It is reasonable, then, to conclude that the acetoxy bromides from **1** will be formed by the same route as that for β-methylstyrenes and will result from anti addition of the solvent molecule. The *E* isomers of **1** (cis vinyl fluorines) lead to formation of the (*R,S*)-("*threo*"[38])-1-acetoxy-2-bromo ad-

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(38) The terms erythro and threo are not strictly applicable for these solvent-incorporated products, but they can be used so that the stereochemistry of the acetoxy and methoxy adducts can be readily compared to the dibromo adducts.

duct. Similarly, the *Z* isomers lead to the *R,R* diastereomers ("erythro").

The formation of the acetoxy bromides from **2** appears to be a stereoselective process. Only one diastereomer could be observed by ^{19}F NMR in the bromination reaction, although an independent synthesis yielded both diastereomers. As the erythro diastereomer is favored for the dibromides, it is assumed that the corresponding (*R,R*)-1-acetoxy-2-bromo adduct is the diastereomer formed in the reaction.

Reaction in Methanol. The reaction of (*E*)-**1d** or (*E*)-**2d** with bromine in methanol to form only the 1-methoxy-2-bromo adduct is similar to the reactions of β-methylstyrenes in methanol where the solvent-incorporated products are predominant[14] and are formed stereospecifically anti.[39]

The ^{19}F NMR of the methoxy bromide adduct from (*E*)-**2d** was more similar to the ^{19}F NMR of the *R,R* acetoxy bromide adduct from **2d** and has been assigned the *R,R* configuration ("erythro"[38]). The methoxy bromide adduct from (*E*)-**1d** has been assigned the *R,S* configuration ("threo"), as this diastereomer would be formed by anti attack of methanol on the intermediate cation. This maintains the relative stereochemistry of the acetoxy and methoxy adducts.

Conclusions

The ionic addition of bromine in acetic acid to the fluorinated styrenes **1**, **2**, and **3** can be summarized as follows. The olefins that do not contain a phenyl substitutent capable of stabilizing a cation (R = CO_2H, Br, H) exhibit reaction product distribution and stereochemistry comparable to those of other styrene derivatives. The 1,2-dibromo adduct predominates, and it is formed by preferential anti addition of bromine which results from partial bromine bridging in the intermediate cation. The olefins that have a phenyl substituent that is electron releasing (R = CH_3, OCH_3) show a dramatic change in product stereochemistry. While the predominant product is still the 1,2-dibromo adduct, it is now formed via preferential syn addition of bromine. This is due to the intervention of a σ complex or an ion pair (with no bromine bridging) that collapses to the syn adduct before substantial ion separation, bromine bridging, or C_α–C_β bond rotation occurs. The amount of syn addition is sensitive to the bromine concentration, to the vinyl substituent on the α-carbon, and to the nature of the phenyl substituent.

Experimental Section

^1H NMR spectra were obtained on a Varian T-60 spectrometer. ^{19}F NMR spectra were recorded on the same instrument operated at 56.4 MHz, and chemical shifts were measured relative to external CF_3CO_2H and converted to ϕ^* values. Mass spectral analysis was performed on a Perkin-Elmer Hitachi RMU-7 double-focusing mass spectrometer at either 70 or 20 eV. *F*-Propene and chloro-*F*-ethene were obtained from PCR Research Chemicals; *n*-butyllithium was obtained from Alfa Ventron. Reagent-grade bromine from Fisher and glacial acetic acid from Baker were used directly as received.

Olefin Preparation. The preparations of $C_6H_5CF{=}CFX$,[40] $4\text{-}BrC_6H_4CF{=}CFX$,[22] and $4\text{-}HO_2CC_6H_4CF{=}CFX$[22] (X = Cl, CF_3) have been reported. The same procedure was used for the preparation of $4\text{-}CH_3C_6H_4CF{=}CFX$ and $4\text{-}CH_3OC_6H_4CF{=}CFX$. The *E* and *Z* isomers of each olefin were separated by preparative GLC on an 8-ft 20% Apeizon-L column.[22,41] The purity of each isomer was verified by analytical GLC analysis and by ^{19}F NMR. Each olefin has a mass spectrum consistent with its structure, and the final *E* or *Z* structure assignment was by ^{19}F NMR (Table V, supplementary material).

The procedure used for the preparation of $4\text{-}RC_6H_4CH{=}CFCl$ (**3**; R = Br, CH_3) was that of Van Hamme and Burton.[24] Thus, to 300 mL of dry DMF was added 60 mmol (7.20 g) of $4\text{-}CH_3C_6H_4CHO$, 70 mmol (18.36 g) of triphenylphosphine, 100 mmol (13.72 g, 8.42 mL) of $CFCl_3$, and 0.316 mol (20.63 g) of zinc dust. The reaction was stirred under nitrogen for 5 days at 60 °C. The mixture was cooled, poured into water, extracted in hexane, washed with water, and dried. The hexane was removed, and the isomeric olefins were separated by preparative GLC on 20% Apeizon-L. The *E* and *Z* isomers were identified by their mass spectra and their ^{19}F and ^1H NMR.[42] (*E*)-$4\text{-}BrC_6H_4CH{=}CFCl$: ϕ^*(F) 70.4, δ(H) 5.61, δ(C_6H_4) 6.9–7.3, *J*(H–F) = 30.1 Hz. (*Z*)-$4\text{-}BrC_6H_4CH{=}CFCl$: ϕ^*(F) 67.3, δ(H) 6.17, δ(C_6H_4) 6.9–7.3, *J*(H–F) = 12.4 Hz. (*E*)-$4\text{-}CH_3C_6H_4CH{=}CFCl$: ϕ^*(F) 73.8, δ(H) 5.53, δ(CH_3) 2.52, δ(C_6H_4) 6.9–7.3, *J*(H–F) = 31.3 Hz. (*Z*)-$4\text{-}CH_3C_6H_4CH{=}CFCl$: ϕ^*(F) 71.0, δ(H) 6.11, δ(CH_3) 2.52, δ(C_6H_4) 6.9–7.3, *J*(H–F) = 13.0 Hz.

Bromination Reactions. a. High Concentration. The reactions were performed in an NMR tube; ca. 0.60 mmol of the olefin was weighed into the tube and 0.25 mL of solvent added, followed by 25 μL (0.50 mmol) of neat bromine. The initial concentration of bromine was ca. 1.4 M. For ionic reactions the tube was wrapped with aluminum foil before the bromine addition and stored in a light-tight box. Radical reactions were irradiated by a 60-W tungsten lamp.

The reaction was stopped by the addition of 75 μL (0.71 mmol) of trimethylethylene. The reaction mixture was then analyzed by ^{19}F NMR. For the reactions of **1** and **3** the product yields and diastereomer ratios were determined by peak area integration or by peak height measurement, which were found to be equivalent. For the reactions of **2** the product yields and ratios were determined from the intensity of the trifluoromethyl resonances.

b. Low Concentration. The reaction vessel was a 25-mL single-necked flask into which was weighed ca. 0.80 mmol of the olefin followed by 10 mL of solvent. Then 5 mL of a 0.10 M bromine solution (0.50 mmol bromine in the appropriate solvent) was added to the flask. The initial bromine concentration was 3.3×10^{-2} M. For the ionic reactions the addition of bromine was done in the dark and the reaction flask was stored in a light-tight box. The radical reactions were irradiated by a 60-W tungsten lamp.

The reaction was stopped by the addition of excess trimethylethylene. For reactions in acetic acid, the mixture was poured into water and extracted into ether, the ether layer was washed and dried with molecular sieves, and the ether was removed. The organic concentrate was diluted with acetone and its ^{19}F NMR spectrum recorded. For reactions in CCl_4, the solvent was removed, and the organic concentrate was diluted with acetone and its ^{19}F NMR recorded.

Dibromo Adducts. Samples of the 1,2-dibromo adducts from **1**, **2**, and **3** were prepared in CCl_4 by reaction with excess bromine and were isolated by simple distillation. Each adduct gave a mass spectrum consistent with its structure. The ^{19}F NMR data of the adducts from **1** and **2** are listed in Table III, and data for the adducts from **3** are as follows. (*R,R*)-$4\text{-}BrC_6H_4CHBrCFClBr$: ϕ^*(F) 50.5, δ(H) 5.77, *J*(H–F) = 11.5 Hz. *R,S* isomer: ϕ(F) 55.2 δ(H) 5.37, *J*(H–F) = 16.4 Hz. (*R,R*)-$4\text{-}CH_3C_6H_4CHBrCFClBr$: ϕ^*(F) 51.2, δ(H) 5.82, δ(CH_3) 2.50, *J*(H–F) = 11.5 Hz. *R,S* isomer: ϕ^*(F) 55.9, δ(H) 5.73, δ(CH_3) 2.50, *J*(H–F) = 16.0 Hz.

NaI Eliminations. The relative configurations of the diastereomeric 1,2-dibromo adducts were confirmed by the E2 elimination of bromine by sodium iodide in acetone.[22,27]

The relative configuration of the adducts from **1** and **2** had been previously established.[22] The configurational assignment was confirmed by the reaction of 0.188 mmol (72 mg) of 4-

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$CH_3C_6H_4CFBrCFBrCF_3$ (erythro/threo ratio of 32:68 by ^{19}F NMR) with 1 g of NaI in 15 mL of refluxing acetone for 4 h. Quantitative GLC analysis (internal standard mesitylene) revealed 0.124 mmol of (*Z*)-4-$CH_3C_6H_4CF{=}CFCF_3$ and 0.063 mmol of (*E*)-4-$CH_3C_6H_4CF{=}CFCF_3$ (total 0.187 mmol, 99% yield) for an *E*/*Z* ratio of 31:69. Under the conditions of the E2 elimination the erythro and threo assignments were confirmed as threo gives the *Z* olefin and erythro yields the *E* olefin. Previous studies have shown that the olefins do not isomerize during the reaction.[22]

The relative configurations of the diastereomeric 1,2-dibromo adducts from **3** were established as follows. It was initially assumed that **3b**, 4-$BrC_6H_4CH{=}CFCl$, preferentially added bromine anti; anti addition to the *E* isomer then yields the *R,S* diastereomer, and the *Z* isomer yields the *R,R* diastereomer. The validity of this assignment was confirmed by the E2 elimination with sodium iodide of 4-$CH_3C_6H_4CHBrCFClBr$ (*R,R*/*R,S* ratio of 34:66 from ^{19}F NMR) to form 4-$CH_3C_6H_4CH{=}CFCl$ (*E*/*Z* ratio of 67:33). E2 elimination from the *R,R* diastereomer leads to the *Z* olefin while the *R,S* diastereomer yields the *E* olefin.

Bromination in Methanol. a. 4-$CH_3C_6H_4CF(OCH_3)CFBrCF_3$. The reaction with (*E*)-4-$CH_3C_6H_4CF{=}CFCF_3$ was performed at low bromine concentration as described above; after 3 days, ^{19}F NMR analysis revealed only one diastereomeric reaction product. Neither 4-$CH_3C_6H_4CFBrCFBrCF_3$ nor the *Z* olefin was formed during the reaction. The product was purified and identified as 4-$CH_3C_6H_4CF^A(OCH_3)CF^BBrCF_3$ by its NMR and mass spectrum: NMR $\phi^*(CF_3)$ 72.7, $\phi^*(F^A)$ 134.3, $\phi^*(F^B)$ 119.7, $J(F^A,F^B)$ = 9.3 Hz, $J(F^A,CF_3)$ = 8.1 Hz, $J(F^B,CF_3)$ = 9.6 Hz, $\delta(OCH_3)$ 3.35, $\delta(CH_3)$ 2.38; mass spectrum (70 eV), *m/e* (relative intensity) 332, 334 (1, $M^{+\cdot}$), 313, 315 (2, $(M - F)^+$), 301, 302 (4, $(M - OCH_3)^+$) 153 (100, $(M - CFBrCF_3)^+$), 119 (33, $CH_3C_6H_4CO^+$).

b. 4-$CH_3C_6H_4CF(OCH_3)CFBrCl$. The reaction was performed with (*E*)-4-$CH_3C_6H_4CF{=}CFCl$ at low bromine concentration as described above; after 3 days, ^{19}F NMR analysis failed to reveal either 4-$CH_3C_6H_4CFBrCFBrCl$ or the *Z* olefin. Only the resonances from one diastereomeric product were observed. The product was purified and identified as 4-$CH_3C_6H_4CF^A(OCH_3)CF^BBrCl$ by its NMR and mass spectrum: NMR $\phi^*(F^A)$ 120.9, $\phi^*(F^B)$ 68.0, $J(F,F)$ = 11.3 Hz, $\delta(OCH_3)$ 3.36, $\delta(CH_3)$ 2.40; mass spectrum (70 eV) *m/e* (relative intensity) 298, 300, 302 (1, $M^{+\cdot}$), 279, 281, 283 (2, $(M - F)^+$), 267, 269, 271 (1, $M - OCH_3)^+$), 153 (100, $(M - CFBrCl)^+$), 119 (55, $CH_3C_6H_4CO^+$).

1-Acetoxy-2-Bromo Adducts. Authentic samples of 4-$CH_3C_6H_4CF(O_2CCH_3)CFBrCF_3$ and 4-$CH_3C_6H_4CF(O_2CCH_3)$-$CFBrCl$ were prepared by reaction of **2d** and **1d**, respectively, with bromine and mercuric acetate in acetic acid.[26] For example, 9.0 mmol (2.0 g) of 4-$CH_3C_6H_4CF{=}CFCF_3$, 20 mmol (6.38 g) of mercuric acetate, and 30 mL of acetic acid were mixed in a flask. Bromine (10 mmol, 1.6 g) was mixed with 5 mL of acetic acid and added to the flask in the dark. The flask was set in a light-tight box for 13 days, after which trimethylethylene was added to remove the excess bromine. The mixture was extracted into ether, the ether layer was washed and dried (molecular sieves), and the ether was removed. The residue was washed with hexane, and the filtrates were combined, concentrated, and flash distilled to yield 1.4 g of product. ^{19}F NMR analysis revealed no unreacted olefin and no 4-$CH_3C_6H_4CFBrCFBrCF_3$. Two diastereomeric products were present and were identified as 4-$CH_3C_6H_4CF$-$(O_2CCH_3)CFBrCF_3$ by their NMR (Table III) and mass spectra: NMR $\delta(O_2CCH_3)$ 1.97, $\delta(CH_3)$ 2.27; mass spectrum (10 eV), *m/e* (relative intensity) 360, 362 (7, $M^{+\cdot}$), 301, 303 (4, $(M - O_2CCH_3)^+$), 119 (100, $CH_3C_6H_4CO^+$).

In a similar manner the diastereomers of 4-$CH_3C_6H_4CF$-$(O_2CCH_3)CFBrCl$ were isolated and identified: ^1H NMR δ-(O_2CCH_3) 1.93, $\delta(CH_3)$ 2.15; mass spectrum (10 eV), *m/e* (relative intensity) 326, 328, 330 (6, $M^{+\cdot}$), 181 (4, $(M - CFBrCl)^+$), 119 (100, $CH_3C_6H_4CO^+$).

On the basis of their ^{19}F NMR, the 1-acetoxy-2-bromo adducts from **1a**, **1b**, **1c**, **2a**, **2b**, and **2c** were identified; however, only the acetoxy bromides from **1a**, **1b**, and **1c** were present in sufficient quantity to allow determination of all of their ^{19}F NMR spectral parameters. The identification of the acetoxy bromides from **2a**, **2b**, and **2c** is based only on the resonance of the trifluoromethyl groups which appear in a unique position.

With the authentic samples of the acetoxy bromides, GLC analysis of the ionic reactions of **1d**, 4-$CH_3C_6H_4CF{=}CFCl$, and **2d**, 4-$CH_3C_6H_4CF{=}CFCF_3$, verified the percent yield of acetoxy bromides that had been previously determined by ^{19}F NMR. This GLC analysis also supported the identification of the acetoxy bromides from **2a**, **2b**, and **2c** by ^{19}F NMR.

Bromination of 4-$CH_3C_6H_4CH{=}CHCH_3$. *cis*- and *trans*-4-$CH_3C_6H_4CH{=}CHCH_3$ were prepared[43] and separated by preparative GLC on 20% Carbowax 20-M at 180 °C. Each isomer was reacted with bromine in acetic acid in the dark at low concentration as described above. ^1H NMR analysis of the product mixture from the cis olefin showed a 64:36 erythro/threo ratio of 4-$CH_3C_6H_4CHBrCHBrCH_3$, and the trans olefin gave a 67:33 erythro/threo ratio. In each case isomerization of the starting olefin was not observed. The erythro and threo dibromo adducts were identified by their ^1H NMR spectra as compared to those of $C_6H_5CHBrCHBrCH_3$[3,13] and 4-$CH_3OC_6H_4CHBrCHBrCH_3$.[13] Erythro isomer: $\delta(CH_3)$ 1.97, $\delta(H_\alpha)$ 4.92, $\delta(H_\beta)$ 4.50, $\delta(C_6H_4)$ 6.8–7.1, $\delta(CH_3C_6H_4)$ 2.32, $J(H_\alpha\text{–}H_\beta)$ = 10.1 Hz, $J(H_\beta\text{–}CH_3)$ = 5.9 Hz. Threo isomer: $\delta(CH_3)$ 1.65, $\delta(H_\alpha)$ 5.14, $\delta(H_\beta)$ 4.47, $\delta(C_6H_4)$ 6.8–7.1, $\delta(CH_3C_6H_4)$ 2.32, $J(H_\alpha\text{–}H_\beta)$ = 5.9 Hz, $J(H_\beta\text{–}CH_3)$ = 6.4 Hz.

Registry No. (*E*)-**1a**, 68423-93-8; (*Z*)-**1a**, 68423-92-7; (*E*)-**1b**, 7422-21-1; (*Z*)-**1b**, 7422-44-8; (*E*)-**1c**, 7422-19-7; (*Z*)-**1c**, 10575-55-0; (*E*)-**1d**, 7422-22-2; (*Z*)-**1d**, 7422-45-9; (*E*)-**1e**, 61855-55-8; (*Z*)-**1e**, 61855-57-0; (*E*)-**2a**, 955-42-0; (*Z*)-**2a**, 68423-94-9; (*E*)-**2b**, 72926-82-0; (*Z*)-**2b**, 72926-83-1; (*E*)-**2c**, 41500-48-5; (*Z*)-**2c**, 41424-70-8; (*E*)-**2d**, 72926-84-2; (*Z*)-**2d**, 72926-85-3; (*E*)-**2e**, 41424-73-1; (*Z*)-**2e**, 41424-33-3; (*E*)-**3b**, 72926-40-0; (*Z*)-**3b**, 72926-41-1; (*E*)-**3d**, 16630-01-6; (*Z*)-**3d**, 16630-00-5; *erythro*-*p*-(1,2-dibromo-2-chloro-1,2-difluoroethyl)-benzoic acid, 68423-95-0; *threo*-*p*-(1,2-dibromo-2-chloro-1,2-difluoroethyl)benzoic acid, 68423-96-1; *erythro*-1-(*p*-bromophenyl)-1,2-dibromo-2-chloro-1,2-difluoroethane, 72926-57-9; *threo*-1-(*p*-bromophenyl)-1,2-dibromo-2-chloro-1,2-difluoroethane, 72926-58-0; *erythro*-1,2-dibromo-2-chloro-1,2-difluoro-1-phenylethane, 68423-99-4; *threo*-1,2-dibromo-2-chloro-1,2-difluoro-1-phenylethane, 68424-00-0; *erythro*-1-(*p*-methylphenyl)-1,2-dibromo-2-chloro-1,2-difluoroethane, 72926-59-1; *threo*-1-(*p*-methylphenyl)-1,2-dibromo-2-chloro-1,2-difluoroethane, 72926-60-4; *erythro*-1-(*p*-methoxyphenyl)-1,2-dibromo-2-chloro-1,2-difluoroethane, 72926-61-5; *threo*-1-(*p*-methoxyphenyl)-1,2-dibromo-2-chloro-1,2-difluoroethane, 72926-62-6; *erythro*-*p*-(1,2-dibromo-1,2,3,3,3-pentafluoropropyl)-benzoic acid, 68423-97-2; *threo*-*p*-(1,2-dibromo-1,2,3,3,3-pentafluoropropyl)benzoic acid, 68423-98-3; *erythro*-1-(*p*-bromophenyl)-1,2-dibromo-1,2,3,3,3-pentafluoropropane, 72938-26-2; *threo*-1-(*p*-bromophenyl)-1,2-dibromo-1,2,3,3,3-pentafluoropropane, 72926-63-7; *erythro*-1,2-dibromo-1,2,3,3,3-pentafluoro-1-phenylpropane, 68424-01-1; *threo*-1,2-dibromo-1,2,3,3,3-pentafluoro-1-phenylpropane, 68424-02-2; *erythro*-1-(*p*-methylphenyl)-1,2-dibromo-1,2,3,3,3-pentafluoropropane, 72926-64-8; *threo*-1-(*p*-methylphenyl)-1,2-dibromo-1,2,3,3,3-pentafluoropropane, 72926-65-9; *erythro*-1-(*p*-methoxyphenyl)-1,2-dibromo-1,2,3,3,3-pentafluoropropane, 72926-66-0; *threo*-1-(*p*-methoxyphenyl)-1,2-dibromo-1,2,3,3,3-pentafluoropropane, 72938-27-3; (*R,S*)-*p*-(1-acetoxy-2-bromo-2-chloro-2,2-difluoroethyl)benzoic acid, 72926-67-1; (*R,R*)-*p*-(1-acetoxy-2-bromo-2-chloro-2,2-difluoroethyl)benzoic acid, 72926-68-2; (*R,S*)-1-(*p*-bromophenyl)-1-acetoxy-2-bromo-2-chloro-1,2-difluoroethane, 72926-69-3; (*R,R*)-1-(*p*-bromophenyl)-1-acetoxy-2-bromo-2-chloro-1,2-difluoroethane, 72926-70-6; (*R,S*)-1-acetoxy-2-bromo-2-chloro-1,2-difluoro-1-phenylethane, 72926-71-7; (*R,R*)-1-acetoxy-2-bromo-2-chloro-1,2-difluoro-1-phenylethane, 72938-28-4; (*R,S*)-1-(*p*-methylphenyl)-1-acetoxy-2-bromo-2-chloro-1,2-difluoroethane, 72926-72-8; (*R,R*)-1-(*p*-methylphenyl)-1-acetoxy-2-bromo-2-chloro-1,2-difluoroethane, 72938-18-2; *p*-(1-acetoxy-2-bromo-1,2,3,3,3-pentafluoropropyl)-benzoic acid, 72926-73-9; 1-(*p*-bromophenyl)-1-acetoxy-2-bromo-1,2,3,3,3-pentafluoropropane, 72926-74-0; (*R,S*)-1-(*p*-methylphenyl)-1-acetoxy-2-bromo-1,2,3,3,3-pentafluoropropane, 72938-29-5; (*R,R*)-1-(*p*-methylphenyl)-1-acetoxy-2-bromo-1,2,3,3,3-pentafluoropropane, 72938-24-0; (*R,S*)-1-(*p*-bromophenyl)-1,2-dibromo-2-chloro-2-fluoroethane, 72938-17-1; (*R,R*)-1-(*p*-bromophenyl)-1,2-dibromo-2-chloro-2-fluoroethane, 72926-42-2; (*R,S*)-1-(*p*-methylphenyl)-1,2-dibromo-2-chloro-2-fluoroethane, 72926-43-3; (*R,R*)-1-(*p*-methylphenyl)-1,2-dibromo-2-chloro-2-fluoroethane, 72926-44-4;

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4-methylbenzaldehyde, 104-87-0; trichlorofluoromethane, 75-69-4; 1-(*p*-methylphenyl)-2-bromo-1-methoxy-1,2,3,3,3-pentafluoropropane, 72926-45-5; 1-(*p*-methylphenyl)-2-bromo-1-methoxy-2-chloro-1,2-difluoroethane, 72926-46-6; (*E*)-1-methyl-4-(1-propenyl)benzene, 2077-30-7; (*Z*)-1-methyl-4-(1-propenyl)benzene, 2077-29-4; *erythro*-1-(*p*-methylphenyl)-1,2-dibromopropane, 72926-47-7; *threo*-1-(*p*-methylphenyl)-1,2-dibromopropane, 72926-48-8.

Supplementary Material Available: Table IV (radical bromination reactions) and Table V (^{19}F NMR data of **1b**, **1d**, **1e**, **2b**, **2d**, and **2e**) (2 pages). Ordering information is given on any current masthead page.

Kinetics and Stereochemistry of the Addition of Chlorine to Styrenes

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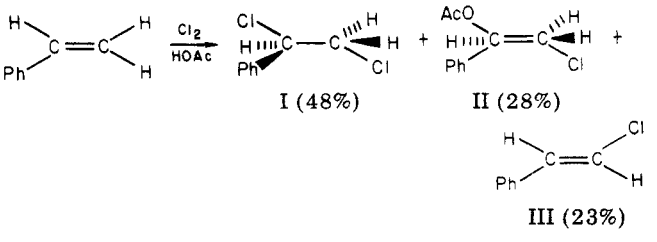
The chlorination of several ring- and side-chain-substituted styrenes has been studied in anhydrous acetic acid, in both the presence and absence of added perchlorate, chloride, and acetate salts. The reactions give three types of product: the 1,2-dichlorides arising from simple addition, 1-acetoxy-2-chloro compounds from addition followed by solvent incorporation, and β-chlorostyrenes from an addition–elimination process. The reactions are completely regiospecific in the Markownikoff sense, and the addition–elimination products are formed with high stereoselectivity. However, both types of addition product are formed nonstereospecifically. Both the product distribution and stereoselectivity are remarkably insensitive to added perchlorate, chloride, or acetate, and very high concentrations of these salts (ca. 1.0 M) are required to produce any significant change in product composition. The results are explicable in terms of a product-determining intermediate which consists of an intimate ion pair between an open β-chlorobenzyl carbonium ion and a tightly held chloride counterion. However, since (*E*)- and (*Z*)-1-phenylpropenes do not give similar product distributions under any conditions used, rotation of the C_α–C_β bond in the carbonium ion must be highly restricted. The rates of reaction have been studied by a combination of potentiometric and stopped-flow spectrophotometric techniques. The reactions are first order in chlorine and first order in olefin and are generally very fast, with most of the rate constants being in the range 10^2–10^5 L mol^{-1} s^{-1}. The rate constants for the ring-substituted styrenes give a good linear correlation against σ^+ with a ρ value of −3.22. This value is less negative than expected from a comparison with other electrophilic additions and is discussed in terms of an earlier transition state with less charge development at C_α than in the analogous bromination reaction. The activation parameters obtained for two of the styrenes support this hypothesis. There is no direct evidence for chlorine bridging at either the transition state or the intermediate stage.

The most thoroughly and systematically studied electrophilic additions of halogens to olefins have involved bromine addition.[1] The kinetics, product distribution, and stereochemistry of bromination of both simple alkenes and alkenes bearing phenyl groups have been investigated by a number of authors.[2] The mechanisms of the corresponding additions of chlorine have been investigated less extensively, largely because the rates of these reactions are much faster than those of the analogous brominations. Most of the mechanistic studies reported so far have dealt with the product distributions and stereochemistry of chlorination of simple alkenes, either involving molecular chlorine[3] or chlorine acetate[4] as the electrophilic species. The rates of these reactions are generally so fast that previous kinetic studies have been restricted either to alkenes containing electron-withdrawing groups[5] or to the determination of relative rates by competition methods.[6] Although the stereochemistry of chlorine addition to various phenyl-substituted olefins has been investigated by several authors,[3] the only kinetic study of the effects of structure on the rates of chlorination involved a limited series of substituted cinnamic acids.[5] It was therefore of interest to investigate more systematically the kinetics and mechanism of chlorine addition to a series of ring- and side-chain-substituted styrenes and to compare the results with directly analogous investigations of similar bromination reactions.[2] These studies have involved both the effects of olefin structure on the rates and the effects of solvent polarity and added nucleophiles on the product distribution and stereochemistry.

Results and Discussion

Product Distribution. Since the most commonly used solvent for studying the kinetics of halogen additions is anhydrous acetic acid,[1] the products of chlorination of styrene itself were first determined in this solvent, with as low concentrations of reactants as practical (ca. 0.1 M) in order to approach the conditions under which kinetic measurements were to be made. The reaction gives three products, which are fairly typical of the chlorination of conjugated olefins in hydroxylic solvents. Addition products, including the dichloride I and solvent-incorporated product II, make up the majority of the product. Although no stereochemical information can be obtained with styrene itself, concerning whether the addition mode is syn or anti, the only solvent-incorporated product



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