Ionic Reaction of Halogens with Terminal Alkenes: The Effect of Electron-Withdrawing Fluorine Substituents on the Bonding of Halonium Ions

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Ionic reactions of terminal alkenes with chlorine (Cl_2), bromine (Br_2), and iodine monochloride (ICl) are sensitive to the alkyl substituents, and the positions and number of vinyl fluorine atoms. These perturbations influence the symmetry of the halonium ion intermediates, which can be determined by the distribution of the Markovnikov to anti-Markovnikov products. A vinyl fluorine on the number-2 carbon favors an unsymmetrical intermediate with greater charge on the number-2 carbon unless the alkyl group is electron withdrawing. A vinyl fluorine on the terminal number-1 carbon favors positive charge development on that carbon unless a resonance stabilizing group is on the number-2 carbon. The symmetry of halonium ions with vinyl fluorines on both carbons-1 and -2 depends primarily on the characteristics of the alkyl substituent. Intermediates range from open-ions with the positive charge on carbon-2, to various bridged species, to open-ions on the terminal carbon.

Introduction

Addition of halogens to alkenes has been widely studied.[1] Electron-rich alkenes such as vinyl ethers[2a] or vinylcyclopropanes[2b] react rapidly with halogen systems by an ionic process. Halogens are slow to react ionically with electron-deficient alkenes and free-radical pathways predominate.[3a,b] Fluorosubstituted terminal alkenes fall in this class and present an interesting situation in electrophilic reactions. The π-bond is unreactive toward electrophiles due to the electron-withdrawing effect of the perfluoroalkyl group and the vinyl fluorines. Knunants and Polishchuck have shown that the π-bond reactivity decreases toward electrophilic reagents as the number of fluorine atoms on the double bond increases.[4] Therefore, carbocation or radical cation intermediates are difficult to generate, yet when they are formed, they are stabilized by the lone pair of electrons on the vinyl fluorine as shown below.[5]

$$R_F CF = CF_2 + E^{\oplus} \longrightarrow$$

E = Electrophile
$R_F = C_n F_{n+1}$
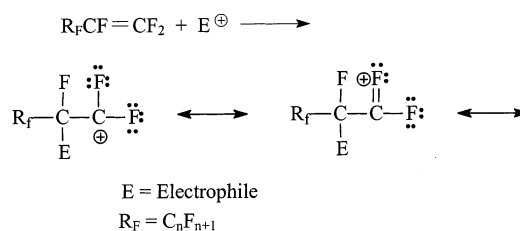
The perfluorocarbon substituent (R_F) above is a strong electron-withdrawing group and cannot participate in resonance stabilization like the electron-withdrawing vinyl fluorine atoms. We recently found that a very slow ionic reaction does occur with chlorine (Cl_2) and perfluoroheptene-1 (**3**) in *tert*-butyl alcohol with mercuric acetate as catalyst.[3b] A smooth ionic reaction occurred with **3** and the reactive electrophile chlorine monofluoride (ClF/N_2) to give only 2-chloroperfluoroheptane, the *anti*-Markovnikov product. Neither bromine (Br_2) nor bromine monochloride (BrCl) was reactive enough to give an ionic reaction with **3**.[3b]

In this paper we report on the ionic additions of halogens to terminal alkenes in methanol, and in some cases in methylene chloride. The regiochemistry of the halomethoxy products from reaction of halogens with hydrocarbon terminal alkenes (**1a,b,c**) from previous studies in methanol is compared to data reported here

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SCHEME 1

R = Electron-withdrawing

2	$R = C_6F_{13}$; $X = Y = Z = H$	
3	$R = R_F = C_5F_{11}$; $X = Y = Z = F$	
8	$R = HCF_2(CF_2)_4$; $X = F$ $Y = Z = H$	

R = Electron-donating   R = Resonance-stabilizing

1a	$R = C_4H_9$; $X = Y = Z = H$	**4**	$R = R_f = C_3F_7O$; $X = Y = Z = F$
1b	$R = C_3H_7$; $X = Y = Z = H$	**4a**	$R = C_3H_7O$; $X = Y = Z = H$
1c	$R = C_6H_{13}$; $X = Y = Z = H$	**6**	$R = Ph$; $X = Y = Z = F$
5	$R = BrCH_2CH_2$; $X = Y = Z = F$	**7**	$R = Ph$; $X = Y = Z = H$
9	$R = C_6H_{13}$; $X = F$, $Y = Z = H$	**10**	$R = Ph$; $X = F$, $Y = Z = H$
11E	$R = C_6H_{13}$; $X = Z = H$, $Y = F$	**12E**	$R = Ph$; $X = Z = H$, $Y = F$
11Z	$R = C_6H_{13}$; $X = Y = H$, $Z = F$	**13E**	$R = Ph$; $X = Z = F$, $Y = H$

when the alkyl group is changed from electron-withdrawing (**2**, **3**, **8**), electron-donating (**1a,b,c**, **5**, **9**, **11***E,Z*), to resonance-stabilizing (**4**, **4a**, **6**, **7**, **10**, **12***E*, **13***E*); (Scheme 1). The vinyl hydrogens are also interchanged to vinyl fluorine atoms. A progressive change in the regiochemistry from Markovnikov (1-halo-2-methoxy, **M**) to *anti*-Markovnikov (2-halo-1-methoxy, **aM**) products (Table 1) reflects on the symmetry of the bonding in the halonium ions as they are captured by methanol in the product-determining (fast) step of the reaction. The intermediates **A** through **E** assigned from these regiochemical data are given in Table 2.

Results and Discussion

Halonium ion symmetry was inferred from the distribution of the halomethoxy products (**M** vs **aM**) by ionic reaction of chlorine (Cl_2), bromine (Br_2), and iodine monochloride (ICl) to alkenes **1a,b,c** through **13***E* in methanol as solvent. Reactions were carried out in the dark and at low concentration of alkene to eliminate a free-radical initation of the electron-deficient alkenes by spontaneous molecule induced homolysis.[3a,6] Data for these reactions are given in Table 1. Some of the dihalo products from alkenes studied were isolated for characterization by a free-radical reaction with halogens in an aprotic solvent (Supporting Information).

Table 2 lists the type of intermediate (**A** through **E**) suggested by the data from the ionic halogenation of terminal alkenes **1a,b,c** through **13***E* in methanol as solvent. Detection of only Markovnikov (**M**) products indicates an open-ion intermediate represented by **A**. Examples of **A** intermediates are those obtained by addition of halogens to vinyl ethers[2a] and vinylcyclopropanes.[2b] The **M** products are from an S_N1-like reaction of the solvent methanol with **A** in the fast second step of the reaction. An intermediate was designated unsymmetrical with the charge localized primarily on carbon-2 as described by halonium ion **B** when a small amount of **aM** product was found, as indicated by a distribution ratio **M/aM** of 2:1 or greater (see Table 1). Product ratios

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(**M/aM**) < 2:1 to 1:6.5 suggest a rather symmetrical intermediate (**C**) similar to that reported for the bromonium ion from 1-hexene[7a] and butadiene monoxide.[7b] The presence of only *anti*-Markovnikov products, or a (**M/aM**) ratio of greater than 1:6.5 indicates an unsymmetrical intermediate like **D** where most of the charge is located on the terminal carbon. The ionic reaction of ClF with perfluoroheptene to give only **aM** products is an example of a reaction where the halonium ion is best represented by **D**.[3b] The intermediate **E** was assigned when no **M** product was observed and a large amount of **aM** solvent incorporated product was found.

Ionic chlorination[8] and bromochlorination (BrCl)[7a] of **1a**, and bromination (Br_2)[9a,b] of **1b** and **1c** in methanol give both **M** and **aM** halomethoxy regioisomers. The **M/aM** ratios are ca. 2–3:1 (Table 1). These data are consistent with an unsymmetrical intermediate with slightly greater charge density on carbon-2 than on carbon-1 described by **B**. A greater amount of **aM** products would be anticipated if the charge distribution on carbons-1 and -2 were similar (**M/aM** ratio 1:>1) since the S_N2-like capture of a symmetrical halonium ion should be favored at the terminal carbon due to steric effects.[9b] We previously described the bromonium ion from **1a** as rather symmetrical.[7a] A better description for the chloronium and bromonium ions from **1a,b,c** would be intermediate **B** or a linear combination of **B** and **C** favoring **B**.

In an earlier paper we reported that $1H,1H,2H$-perfluorooctene-1 (**2**) and perfluoroheptene-1 (**3**) react slowly and give only the *anti*-Markovnikov products[3b] (Table 1). The strong electron-withdrawing perfluoroalkyl substituents destabilize charge development on carbon-2 of the halonium ions from **2** and **3**. Thus the intermediate for these reactions can best be represented by **D** (Table 2).

Substituting the perfluoroalkyl group of **3** with a perfluoroether group, as in **4**, provides an alkene that reacts with halogens in methanol via a bridged halonium ion. Evidence to confirm an ionic pathway for these reactions includes the incorporation of a methoxy group in the products from the solvent methanol and formation of both regioisomers via a halonium ion intermediate as shown in Scheme 2.

The Markovnikov (**M**) product predominates for the reaction of chlorine and **4**; the *anti*-Markovnikov (**aM**) regioisomer is the major product for reaction with bromine, and is the overwhelming product when iodine (ICl) is the electrophile (Table 1). These results indicate a more tightly bridged (with carbon-2) halonium ion for iodine than bromine and, apparently, chlorine has little bridging. The iodonium ion is best described by **D**, the bromonium ion by **C**. and the chloronium ion by **B**. The perfluorovinyl (**4**) progresses from intermediates **B**, **C**, to **D** as the electrophile changes from chlorine, to bromine, to iodine.

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TABLE 1. Reaction of Halogens (Cl_2, Br_2) and Iodine Monochloride (ICl) with Terminal Alkenes in Methanol at 25 °C

	alkene	halogen	dihalo	1-halo-2-methoxy (**M**)	2-halo-1-methoxy (**aM**)	product distribution ratio **M**: **aM**
1a	$C_4H_9CH{=}CH_2$	Cl_2[a]	13	63	24	2.6:1
1b	$C_3H_7CH{=}CH_2$	Br_2[b]	51	37	12	3.1:1
1c	$C_6H_{13}CH{=}CH_2$	Br_2[b]	51	37	12	3.1:1
1a	$C_4H_9CH{=}CH_2$	BrCl[c]	49[d]	34	17	2.1:1
2	$C_6F_{13}CH{=}CH_2$	Cl_2[e]	28		72	**aM** only
2		Br_2[e]	9		91	**aM** only
2		ICl[e]	5		95	**aM** only
3	$C_5F_{11}CF{=}CF_2$	Cl_2[e]	96		4[f]	**aM** only
4	$C_3F_7OCF{=}CF_2$	Cl_2	49	36	15	2.4:1.0
4		Br_2	60	4	33	1.0:4.7
4		ICl	$-$[g]	7	93	1.0:13
5	$BrCH_2CH_2CF{=}CF_2$	Cl2	57	14	29	1.0:2.1
5		Br	25	10	65	1.0:6.5
5		ICl	<1[h]	10	90	1.0:9.0

	alkene	halogen	dihalo	1-halo-2-methoxy (**M**)	2-halo-1-methoxy (**aM**)	product distribution ratio **M**:**aM**
6	$PhCF{=}CF_2$	Cl_2	4	96		**M** only
6		Br_2	20	79	1	79:1.0
6		ICl	25[i]	75		**M** only
7	$PhCH{=}CH_2$	ICl	14[h]	86		**M** only
8	$HCF_2(CF_2)_4CF{=}CH_2$	Cl_2	99		<1	**aM** only
9	$C_6H_{13}CF{=}CH_2$	Cl_2	12	78[j]		**M** only
		Br_2	55	45[k]		**M** only
10	$PhCF{=}CH_2$	Cl_2	6	94[l]		**M** only
10		Br_2	4	96[m]		**M** only
10		ICl		100[n]	$-$[o]	**M** only
11E,Z	$C_6H_{13}CH{=}CHF$[p]	Cl_2	30[q]		70[r]	**aM** only
11E,Z		Br_2	50[q]	5[s]	45[s]	1:9
11E,Z		ICl	30[q]	10[t]	60[u]	1:6
12E	$PhCH{=}CHF$	Cl_2	4[q]	96[v]		**M** only
12E		Br_2	28[w]	72[w]		**M** only
12E		ICl	100[x]			**M** only

	alkene	halogen	dihalo	1-halo-2-methoxy (**M**)	2-halo-1-methoxy (**aM**)	product distribution ratio **M**:**aM**
13E	$PhCF{=}CHF$	Cl_2	11[y]	89[z]		**M** only
13E		Br_2	36[aa]	64[bb]		**M** only
13E		ICl	14[h]	86[cc]		**M** only

[a] Reference 8. [b] Reference 9. [c] Reference 7. [d] Equal amounts of **M** and **aM** bromochloro products were detected. [e] Reference 3b. [f] Solvent *tert*-butanol since methanol is oxidized by Cl_2 in this very slow reaction. See ref 3b. [g] No iodochloro products were formed. [h] **M**, product only. No **aM**, product detected. [i] In methylene chloride as solvent the dihalo-**M**:**aM** ratio was 66:34. [j] Isolated after workup as 1-chloro-2-octanone. Elimination products, chloroalkenes, make up 10% of the reaction mixture. They are 1-chloro-2-fluorooct-1-ene [*E:Z* (1.9:1.4%)] and 1-chloro-2-fluorooct-2-ene [*E:Z* (5.1:1.6%)]. [k] The bromomethoxy product was isolated after workup as 1-bromo-2-octanone. Elimination products were less than 1% of the mixture. [l] Isolated after water workup as a mixture of α-chloroacetophenone and 1-chloro-2,2-dimethoxy-2-phenylethane (14:1). In methylene chloride as solvent 2-chloro-1-fluoro-1-phenylethylene and 1,2-dichloro-1-fluoro-1-phenylethane were formed in 70% yield by NMR in a 55:45 ratio, respectvely. [m] The 1-bromo-2-methoxy product undergoes solvolysis during water workup to α-bromoacetophenone. The alkene 2-bromo-1-fluoro-1-phenylethene was not observed even in methylene chloride as solvent. [n] The isolated products are α-iodo- and α-chloroacetophenone (3:1). [o] No α-methoxyacetophenone, a commercial product, was formed. The α-chloroacetophenone is from Cl_2 formed in slow reactions with ICl. [p] Alkene prepared as an *E:Z* 87:13 mixture. See ref 13. [q] The 1,2-dihaloproducts undergo solvolysis at the terminal carbon. The reaction is not stereospecific in methylene chloride as solvent. [r] Isolated as a mixture of 2-chlorooctanal and 2-chloro-1,1-dimethoxyoctane (1:4) after water workup. [s] Isolated as a mixture of 2-chloro-1-fluoro-1-iodooctane and 2-bromo-1,1-dimethoxyoctane (10:1) after water and workup. [t] Isolated as a mixture of 2-chloro-1-fluoro-1-iodooctane and 2-chloro-1,1-dimethoxyoctane. [u] Isolated as 2-iodo-1,1-dimethoxyoctane, decomposes on standing. [v] Erythro/threo 79:17 by GC analysis. Chlorination is not stereospecific in methanol. [w] Reaction is stereospecific. [x] Reaction run in methylene chloride since methanol gave poor results with numerous unidentified products. In methylene chloride only **M** was formed and the reaction was stereospecific. [y] Loss of stereochemistry. [z] Isolated as 2-chloro-1,2-difluoro-1-methoxy-1-phenylethane (erythro/threo 8:1). [aa] Reaction is not stereospecific in methanol or methylene chloride as solvent. [bb] Isolated as 2-bromo-2-fluoro-1,1-dimethoxy-1-phenylethane. [cc] Isolated as 2-fluoro-1,1-dimethoxy-2-iodo-1-phenylethane. The reaction is stereospecific in methanol and methylene chloride as solvent.

Product distributions with alkene **5** (Table 1), where the alkyl group is a hydrocarbon and the alkene contains three vinyl fluorines, show an increase of the **aM** products progressing from Cl_2 to ICl. At first glance this trend seem at odds with our previously reported data[2a,7ab] and with the other alkenes reported here. Apparently the bromine of alkene **5** captures the halonium ion intermediate to give a five-membered ring that opens to give primarily **aM** products (Scheme 3). A three-membered-ring chloronium ion would have little charge on the terminal carbon and react mainly by the fast-step k_2 (Scheme 3). Bromonium and iodonium ions would progressively bridge better thereby placing more positive charge on the terminal carbon, respectively. The fast-step (k_3) would be most efficient with the iodonium ion and progressively less efficient with bromine to chlorine.

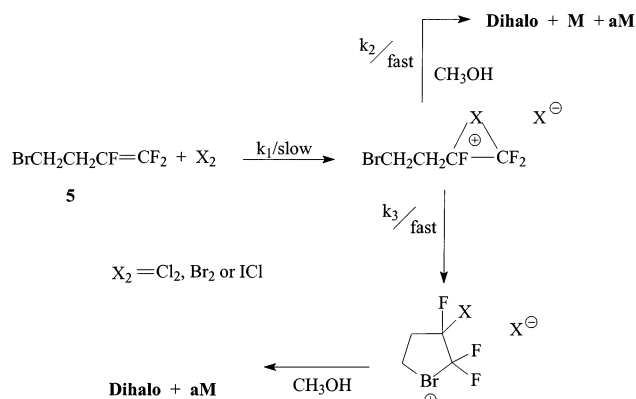**TABLE 2. Halonium Ion Symmetry (Bonding) in Methanol as Solvent**

X = Cl, Br or I

halogen	M only	M/aM 2:1	M/aM <2:1 to 1:6.5	M/aM 1:>6.5	aM only
Cl$_2$	**6, 7, 9, 10, 12, 13**	**1a,b,c, 4, 5**		**2, 3, 8**	**11**
Br$_2$	**7, 9, 10, 13**	**1a,b,c, 6, 12**	**4, 5**	**2, 11**	
ICl	**7, 9, 10**	**6, 12, 13**		**2, 4, 5, 11**	

SCHEME 2

SCHEME 3

SCHEME 4

F	X = Cl;	Y = F
G	X = Cl, Br or I;	Y = H
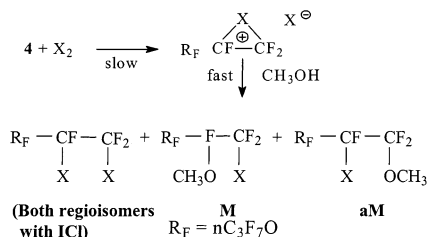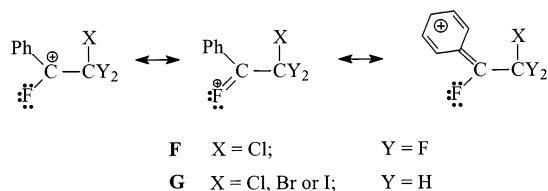
Thus product ratios (**M:aM**) are inversely representative of the three-ring halonium ion symmetry. We suggest the chloronium ion from **5** is best represented by **B**, the bromonium ion by **C**, and the iodonium ion as **D**.

α,β,β-Trifluorostyrene (**6**) forms weakly bridged halonium ions (**B**) with bromine and iodine electrophiles as indicated by the small amount of **aM** products from Br$_2$ and the decrease in halomethoxy products (Table 1). Even though no **aM** iodomethoxy product was detected in methanol, a bridged iodonium was indicated in methylene chloride as solvent by the large amount (34%) of 2-chloro-1-iodo-1,2,2-trifluoro-1-phenylethane **aM** product. Reaction of **6** with chlorine appears to give an open-ion intermediate (**F**, Scheme 4) as indicated by the absence of any **aM** product and the large amount of
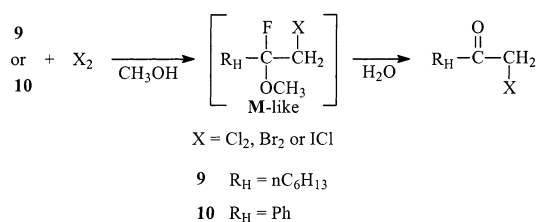
solvent incorporated product relative to the dihalo product (Table 1). We independently synthesized the **aM** product from the photochemical reaction of **6** with methylhypochlorite. Control experiments confirm that the **aM** product is stable to the ionic reaction conditions and would have been detected if formed during the ionic process.

The bridged halonium ions (Cl, Br, I) found for perfluorovinyl ether **4** and the bridged bromonium and iodonium ions from the trifluorostyrene **6** are in contrast to their hydrocarbon analogues. We treated propyl vinyl ether **4a** with Cl$_2$ in methanol to look for the **aM** product. Reaction of **4a** in methanol with Br$_2$ or ICl did not give thermodynamically stable products. Careful analysis of the crude product mixture from chlorination of **4a** in methanol by capillary GC/MS gave no indication of any **aM** product. Ingold and Smith reported a small amount of **aM** product for the ionic reaction of ICl with styrene (**7**).[10] We also reinvestigated this reaction with ICl in methanol and methylene chloride as solvent since iodine electrophiles have the best chance of forming bridged intermediates. Careful analysis of the crude mixture by NMR gave no indication of any kinetically formed **aM** product. The **aM** product was obtained by reaction of PI$_3$ with 2-chloro-1-phenylethanol, and control experiments showed that the **aM** product was stable to the ionic reaction conditions. The **aM** product was not formed during the reaction. Thus our data suggest that the hydrocarbon styrene (**7**) does not give a bridged iodonium intermediate. These findings are also consistent with those reported for the iodochlorination of styrene in methylene chloride or methanol where none of the **aM** regioisomer was reported.[11,12] The large amount of solvent incorporation (86%) for reaction of ICl with styrene (**7**) in methanol is also consistent with an open-ion intermediate. Since iodine supports bridged halonium ions better than bromine or chlorine, it is reasonable to assume that chlorine and bromine also form open-ion intermediates with styrene (**7**). The intermediates for the hydrocarbon alkenes such as propyl vinyl ether (**4a**) and **7** are represented by the open-ion **A** (Table 2).

Alkenes **8**, **9**, and **10** have two hydrogens on the terminal carbon and a fluorine on the internal alkene (number-2) carbon. Data for the ionic reaction of halogens with these three alkenes are also given in Table 1. Reaction of chlorine with **8**, an alkene with a perfluoro-

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SCHEME 5

$$9 \text{ or } 10 + X_2 \xrightarrow{CH_3OH} \left[R_H\text{-}\underset{OCH_3}{\overset{F \quad X}{C}\text{-}CH_2} \right]_{M\text{-like}} \xrightarrow{H_2O} R_H\text{-}\underset{X}{\overset{O}{C}}\text{-}CH_2$$

X = Cl$_2$, Br$_2$ or ICl

9   R$_H$ = nC$_6$H$_{13}$

10   R$_H$ = Ph

SCHEME 6

$$11 + ICl \xrightarrow{CH_3OH} \underset{Cl}{C_6H_{13}CH\text{-}CHF} + \left[\underset{X \quad Y}{C_6H_{13}CH\text{-}CHF} \right]$$

$$\underset{30}{}$$

X = I or Cl

Y = I, Cl, or OCH$_3$

$$\downarrow CH_3OH$$

$$\underset{60}{C_6H_{13}CH\text{-}\underset{I}{CH}\text{-}CH(OCH_3)_2} + \underset{10}{C_6H_{13}\underset{Cl}{CH}\text{-}CH(OCH_3)_2}$$

carbon substituent, was run in *tert*-butyl alcohol, rather than methanol, since the reaction was slow and methanol was oxidized by Cl$_2$. Alkene **8** does not react ionically with Br$_2$ or ICl. We were unable to isolate the small amount of solvent incorporated **aM** product, and an attempted synthesis of the **aM** product by a free-radical process with *tert*-butylhypochlorite proved futile. We have only GC/MS data for this trace product. The trace amount of **aM** product suggests an unsymmetrical intermediate **D** for this reaction.

Alkenes **9** and **10** with hydrocarbon alkyl or phenyl groups and a vinyl fluorine on the internal (number-2) carbon react readily with halogens by an ionic pathway in methanol to give **M**-like products that rapidly solvolyze to 1-haloketones on workup with water (Scheme 5).

No 1-methoxy-2-octanone, an indicator of **aM** addition, from reaction of Cl$_2$ or Br$_2$ with **9** in methanol was found. The reaction of ICl with **9** in methanol was too messy to yield meaningful data. Reaction of α-fluorostyrene (**10**) with Cl$_2$ and Br$_2$ gave only the 1-haloketones after water workup. 2-Methoxyacetophenone, a commercial compound, would have been detected if any **aM**-addition had occurred. Ionic reaction of ICl with **10** was slow (overnight) and the iodoketone from the **M** product was produced but again no 2-methoxyacetophenone from **aM**-addition was detected. 2-Chloroacetophenone was formed in the ICl reaction from the dichloro product. The 2-chloroacetophenone was due to Cl$_2$ generated from disproportionation of ICl during the slow reaction with unreactive alkenes such as **10**. We do not believe that any **aM**-addition occurred from the ionic halogenation of alkenes **9** or **10** although a weakly bridged iodonium ion (**B**) cannot be ruled out by our data. However, the ionic reaction of ICl with **10** in methylene chloride does not support a bridged species since no **aM** product was formed in that reaction. One might anticipate that **9**, and perhaps even **10**, could give a weakly bridged halonium ion since the vinyl fluorine is electron withdrawing and should thereby destabilize the kinetic transition state. Apparently, resonance stabilization by the fluorine in the intermediate from **9** and the fluorine and phenyl ring in **10**, illustrated by **G** (Scheme 4), induces these alkenes to react via an open-ion **A**.

Alkenes **11E**, **11Z**, and **12E**[13] have a single fluorine on the terminal carbon and these alkenes potentially offer both regio- and stereochemical data for interpretation. Ionic reaction of Cl$_2$, Br$_2$, and ICl with **11** in methanol gave products from solvolysis of the 1-halo-1-fluoro product. In methylene chloride reactions of Cl$_2$, Br$_2$, and ICl with **11** were not stereospecific (Table 1). The iodonium ion and the bromonium ion from **11** can best be represented by **D** since there are small amounts of M products formed (Table 1). In methylene chloride both Br$_2$ and ICl react with **11E,Z** (87:13) to give erythro/threo
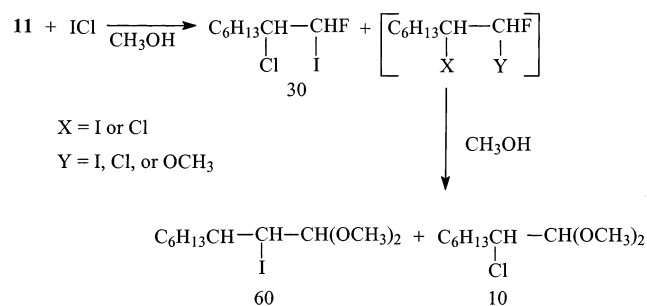
product distributions of 37:63 and 5:95, respectively. These data suggest that there may be an equilibrium between **D** and the open-ion **E** for the bromonium and iodonium ions from **11E,Z** in aprotic solvents. Chlorination of **11E,Z** in methanol gives only **aM**-type products (Table 1). In methylene chloride the threo isomer is also preferred (ca. 95%, see Supporting Information). The absence of any **M**-type products (Table 1) and the loss of stereochemistry in methylene chloride suggest an open-ion intermediate **E** for chlorination of **11E,Z**. Alkene **11E,Z** is an interesting substrate in that positive charge is inductively destabilized on carbon-2 by the terminal fluorine, which then goes on to stabilize charge development on carbon-1 through back-bond resonance. Ionic chlorination of **12E** is not stereospecific in methanol and the large amount of solvent incorporation suggests open-ion **A** for its intermediate. Bromination of **12E** in methanol was stereospecific and the 72% solvent incorporation for bromination suggests intermediate **B**. Reaction of ICl with **12E** in methanol was messy and gave numerous unidentifiable products. In methylene chloride only the **M** product was formed and the reaction was stereospecific. The iodonium ion from **12E** is represented by **B** since the reaction is stereo- and regiospecific. The phenyl group of **12E** obviates the effect of the terminal fluorine observed for **11E,Z** above.

Chlorination and bromination of **13E** are not stereospecific and their intermediates are open-ions, represented by **A**. Ionic reactions of ICl with **13E** in methanol and methylene chloride are stereospecific and therefore are represented by intermediate **B**.

We have shown that the bonding and symmetry of halonium ions from terminal alkenes are sensitive to the alkyl substituents and the position and number of vinylfluorines. A single vinyl fluorine on the number-2 carbon favors positive charge development on that carbon (alkenes **6**, **9**, **10**, **13**) unless a strong electron-withdrawing group (alkene **8**) is on the carbon-2. For example, **aM** products are formed for ionic halogenation of alkenes **1a**, **1b**, and **1c** but not with the fluoroalkene **9**. A fluorine on the terminal carbon favors positive charge development on the terminal carbon (alkene **11E,Z**) unless a resonance stabilizing group is on the number-2 carbon (alkene **12E**). The same trend was found with three vinyl fluorines on the terminal alkene in that the positive charge is on the terminal carbon (alkene **3**, iodonium ion from **5**) unless the number-2 carbon contains a resonance stabilizing substituent (alkenes **4**, **6**) or neighboring group substituent as for the chloronium and bromonium ions from alkene **5**. These perturbations change the symmetry of the halonium ion intermediates and are

responsible for the regiochemistry from ionic halogenation of terminal alkenes containing vinyl fluorines.

Experimental Section

Materials. Alkenes **8**,[14] **9**,[15] **10**[15], **11***E*,*Z*,[13] **12***E*,[13] and **13***E*[16] were synthesized from literature procedures. The remaining chemicals were from major supply firms.

General Procedure for Reaction of Chlorine, Bromine, or Iodine Monochloride with Alkenes. Chlorine was added as a gas, bromine as a neat liquid, and iodine monochloride as a solid. Radical inhibitors (O_2 gas for Cl_2; O_2 gas and isoamyl nitrite for Br_2 ICl) were utilized to obtain analytical data (Product distributions, Table 1) from unreactive alkenes **2**, **3**, and **8** to circumvent a free-radical process via molecule-induced homolysis.[3a,b,6] Product distributions (Table 1) were also obtained with the halogen or interhalogen (ICl) as limiting reagent (50−80% alkene consumed). The procedures for the ionic chlorination of **4** and the free-radical bromination of **5** are representative. Free-radical reactions were useful for the preparation of the dihalo products. Procedures that differ from this general procedure and spectra of new compounds are in the Supporting Information.

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Ionic Reaction. To 133 mg (0.500 mmol) of **4** in 2.2 mL of anhyd methanol was slowly bubbled Cl_2 gas until 80% of the alkene was consumed. Analysis by GC with perfluorooctyl bromide as internal standard (added as 1.0 M CH_2Cl_2, 0.100 mL) gave a 68% yield and the product distribution in Table 1. Products were obtained pure (>98% by GC) by preparative GC with Column A. Spectral data for the dichloro- and chloromethoxy products are given in the Supporting Information.

Free-Radical Reaction. To 1.89 g (10.0 mmol) of neat **5** at 0 °C with stirring and ultraviolet illumination from a 300-W light bulb was added dropwise 1.60 g (10.0 mmol) of neat bromine. Bulb-to-bulb distillation at 68 Torr gave 3.27 g (94% yield) of 1,2,4-tribromo-1,1,2-trifluorobutane. Fractional distillation gave an analytical sample (88−89 °C at 20 Torr) that was found to be 99% pure by GC analysis. Spectral data are given in the Supporting Information.

Supporting Information Available: NMR and mass spectral data of new compounds and references for known compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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