# Rearrangement of 3-Membered 1,1,2-Trifluorobromonium and Iodonium Ions and Comparison of Trifluorochloronium to Fluorocarbenium Ions

Dale F. Shellhamer,[†] Kevyn J. Davenport,[†] Heidi K. Forberg,[†] Matthew P. Herrick,[†]
Rachel N. Jones,[†] Sean J. Rodriguez,[†] Sunamita Sanabria,[†] Nicole N. Trager,[†]
Ryan J. Weiss,[†] Victor L. Heasley,[†] and Jerry A. Boatz*,[‡]

*Department of Chemistry, Point Loma Nazarene University, San Diego, California 92106-2899, and Air
Force Research Laboratory, Edwards Air Force Base, California 93524-7680*

dshellha@pointloma.edu

Received February 28, 2008
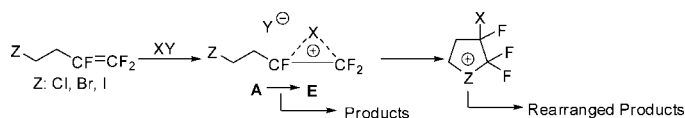
Reactions of chlorine (Cl_2) with 4-halo-1,1,2-trifluorobut-1-enes (**1**, **2**, or **3**) give open-ion intermediates **A** and **E** that are in equilibrium. The open-chloronium ions (**E**) rearrange to a five-membered-ring halonium ion during ionic chlorination of **3** when the number-4 halo-substituent is iodine. Three-membered-ring bromonium and iodonium ions from alkenes **1**, **2**, or **3** are rather symmetrical and similar in structure. Quantum chemical calculations show that five-membered-ring halonium ion intermediates are 11 to 27 kcal/mol more stable than the three-membered-ring halonium ions or the open-ions **A** and **E**. The five-membered-ring intermediates lead to rearranged products. Rearranged products increase as the number-4 halogen (Z) becomes more nucleophilic (Z: Cl < Br < I). Open chloronium ions from ionic chlorination of terminal fluorovinyl alkenes are compared to the open ions generated by protons to similar alkenes.

Introduction

In an earlier study we reported on the structure and symmetry of halonium ion intermediates from fluorosubstituted terminal alkenes.[1] Structures for these intermediates were assigned based on the distribution of Markovnikov (**M**) to *anti*-Markovnikov (**aM**) products when the halonium ions were opened by the solvent methanol. These assignments were refined by quantum chemical calculations to include structures expected in the gas phase and from the solvent effects in methanol.[2] Halonium ion structures were found to be open-ion (**A** or **E**), unsymmetrical (**B** or **D**), or symmetrical **C** depending on the halogen electrophile and on the position and number of vinylfluorines bonded to the terminal alkene.[1,2] Structures for the three-membered halonium ions were assigned from bond angles obtained by quantum chemical calculations.[2] The bond angle X–C_1–C_2 (α)
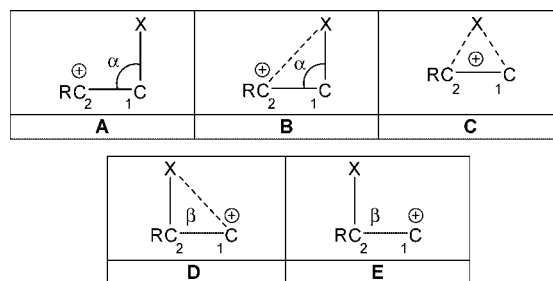
gave the best description for halonium ion structures **A** and **B**, while the X–C_2–C_1 bond angle (β) gave accurate descriptions for **D** and **E**.[2] Bond angles around 55–60° for α or β represent structure **C**.[2] Data from halogenation reactions of 4-bromo-1,1,2-trifluorobut-1-ene (**2**) were explained by neighboring group participation from the number-4 bromine with the three-membered halonium ion intermediate to give a five-membered ring trifluorotetramethylene bromoniun ion **5** (Scheme 1, Z = Br).[1] The steric effect and repulsive forces from the lone-pair electrons on the fluorine atoms of **5** shield the carbon nucleus, rendering it resistant to nucleophilic displacement.[3] Thus, when the five-membered ring intermediate is formed, attack by the
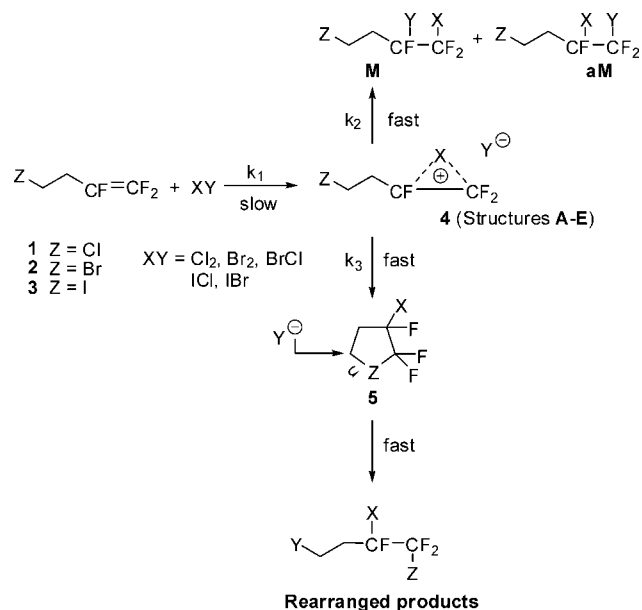
[†] Point Loma Nazarene University.
[‡] Edwards Air Force Base.
(1) Shellhamer, D. F.; Allen, J. L.; Allen, R. D.; Gleason, D. C.; O'Neil Schlosser, C.; Powers, B. J.; Probst, J. W.; Rhodes, M. C.; Ryan, A. J.; Titterington, P. K.; Vaughan, G. G.; Heasley, V. L. *J. Org. Chem.* **2003**, *68*, 3932.
(2) Shellhamer, D. F.; Gleason, D. C.; Rodriguez, S. L.; Heasley, V. L.; Boatz, J. A.; Lehman, J. J. *Tetrahedron* **2007**, *62*, 11608.

SCHEME 1

TABLE 1. Halonium Ion Bond Angles (α, β) and Charge Densities (C_1, C_2)[a]

				bond angle		charges		structure[b]
				C_2-C_1-X	$X-C_2-C_1$	Q	Q	based on bond
run	Z	X	Y	(α)	(β)	(C_2)	(C_1)	angle α
1a	Cl	Cl	Cl	93.8	47.4	+0.18	−0.07	**A**
1b	Cl	Cl	Cl	50.8	89.6	−0.11	+0.19	**E**
2	Cl	Br	Br	68.3	71.2	−0.03	+0.05	**C⇒D**
3	Cl	I	Br	70.2	73.4	−0.08	+0.02	**C⇒D**
4	Br	Cl	Cl	94.0	47.3	+0.18	−0.07	**A**
5	Br	Br	Cl	68.2	71.3	−0.03	+0.05	**C⇒D**
6	Br	I	Cl	70.0	73.5	−0.08	+0.02	**C⇒D**
7a	I	Cl	Cl	94.6	46.9	+0.18	−0.07	**A**
7b	I	Cl	Cl	50.9	89.4	−0.11	+0.19	**E**
8	I	Br	Br	68.1	71.4	−0.03	+0.05	**C⇒D**
9	I	I	Br	69.9	73.7	−0.08	+0.02	**C⇒D**

[a] Geometries were calculated at the MP2/6-311++G(P,d) level theory. Lodwin atomic charges were obtained by using a Mulliken population analysis based upon symmetrically orthogalized orbitals. [b] Structures **A** through **E** are shown in the Introduction. The symbol **C⇒D** means that the halonium ion is rather symmetrical like **C** with some asymmetry approaching structure **D**.

nucleophile will be at the hydrocarbon rather than the fluorocarbon methylene of **5**. These rearranged products (Scheme 1) provide experimental evidence for formation of the tetramethylene halonium ion intermediates. Neighboring group participation is well-known, and anchimeric acceleration is greatest for formation of five-membered rings.[4]

In this paper we investigate the influence that a 4-halosubstituent has on formation of three-membered halonium ions and their rearrangement to five-membered-ring intermediates when chloronium, bromonium, and iodonium ions from alkenes **1**, **2**, and **3** are formed in aprotic solvent (Scheme 1). We also compare the open-ion chloronium ions with the open-carbocations from addition of a proton to terminal fluorosubstituted alkenes. Ohta has shown by ^{13}C NMR isotope shift studies that hydrocarbon chloronium and bromonium ions can open to β-halocarbenium ions in super acid.[5]

$$ZCH_2CH_2CF=CF_2$$
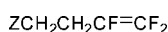
1 Z = Cl
2 Z = Br
3 Z = I

Results and Discussion

A. Comparing the Effect of the Number-4 Substituent (Z) on Intermediates from Alkenes 1, 2, and 3. (1) Halonium Ions from 1. Quantum chemical calculations indicate an open-ion structure **A** for the intermediate from reaction of chlorine with alkene **1** (Table 1, run 1). Reaction of chlorine (Cl_2) with **1** cannot provide experimental evidence for a five-membered-ring intermediate since migration of the 4-chlorosubstituent cannot be discerned because intermediates **4** and **5** (Scheme 1, X = Y = Z = Cl) each react with chloride ion to give the same product 1,2,4-trichloro-1,1,2-trifluorobutane (**8**). The parent hydrocarbon tetramethylene chloronium ion has been

reported in the gas phase,[6] in superacid media,[7] and for the addition of trifluoroacetic acid to 5-chloro-1-hexene.[8] The five-membered trifluorochloronium ion **5** (Scheme 1, X = Y = Z = Cl) is 19.7 kcal/mol more stable than the open-chloronium ion **A** (Table 2, run 1). Calculations also show that the open-chloronium ion **E** is only 1.4 kcal/mol less stable than **A** (Table 2, run 1). If the five-membered-ring **5** (Scheme 1, X = Y = Z = Cl) is formed, then it is from intermediate **E** in equilibrium with **A**. Our data show that a rearranged product through step 3 in Scheme 1 is plausible, but we suspect that formation of **5** (Scheme 1, X = Y = Z = Cl) does not occur. Only 2% rearranged product was found for chlorination of alkene **2** where the number-4 halogen is bromine (Table 3, run 5). We would expect very little rearrangement of the open-chloronium ion **E** when the number-4 halogen is the less nucleophilic chlorine.

Bond angle data in Table 1 show that the three-membered-ring bromonium and iodonium ions from alkene **1** resemble structure **C** with some small asymmetry like **D** written as **C⇒D**[2] (Table 1, runs 2 and 3). Rearranged products from five-membered-ring halonium ions **5** were not observed for reactions of bromine (Br_2), bromine monochloride (BrCl), or iodine monobromide (IBr) with alkene **1** (Table 3, runs 2, 3, and 4). These data show that the number-4 chlorine atom in alkene **1** does not function as a neighboring group participant with either the three-membered bromoniun or iodonium ions even though the five-membered-ring intermediates are more stable by 16.2 and 11.6 kcal/mol, respectively (Table 2, runs 2 and 3).

(2) Halonium Ions from 2. Electrophilic addition of Cl_2 to alkene **2** gives 2% of rearranged product (Table 3, run 5). Intermediate **5** (Scheme 1, X = Y = Cl; Z = Br) is 22.1 kcal/mol more stable than the open-ion **A** (Table 2, run 4). Our calculations did not find a local minimum **E** for an open-

(3) Banks, R. E.; Smart, B. E., and Tatlow, J. C., Eds. Organofluorine Chemistry. Principles and Commercial Applications. In *Topics in Applied Chemistry*; Plenum Press: New York, 1994; pp 71 and 190. Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley: New York, 1973; p 98.
(4) (a) Heine, H. W.; Siegfried, W. *J. Am. Chem. Soc.* **1954**, *76*, 489. (b) Swain, C. G.; Kuhn, D. A.; Schowen, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 1553.
(5) Ohta, B. K.; Hough, R. E.; Schubert, J. W. *Org. Lett.* **2007**, *9* (12), 2317.

(6) Van de Sande, C. C.; McLafferty, F. W. *J. Am. Chem. Soc.* **1975**, *97*, 2298.
(7) Olah, G. A. *J. Am. Chem. Soc.* **1968**, *90*, 4675.
(8) Peterson, P. E.; Tao, E. V. P. *J. Am. Chem. Soc.* **1964**, *86*, 4503.

TABLE 2. MP2/6-311++G(D,P) Relative Enthalpies^a (ΔH_o, kcal/mol)

Run	Z	X	Y	C ⇒ D bridged (kcal/mole)	open-ion (kcal/mole) A	open-ion (kcal/mole) E	five-membered ring
1	Cl	Cl	Cl		19.7[b]	21.1[b]	0
2	Cl	Br	Br	16.2			0
3	Cl	I	Br	11.6			0
4	Br	Cl	Cl		22.1	...[c]	0
5	Br	Br	Cl	18.6			0
6	Br	I	Cl	14.0			0
7	I	Cl	Cl		25.7[b]	27.3[b]	0
8	I	Br	Br	22.2			0
9	I	I	Br	17.6			0

^{a} Zero-point vibrational energy corrections scaled by 0.9748 (see:. Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513). ^{b} Two stable open-ion structures were found, resembling structures **A** and **E**. ^{c} Did not find an open-ion local minimum for **E**.

TABLE 3. Products from Reaction of 4-Halo-1,1,2-trifluorobut-1-enes (1, 2, and 3) with Halogen Electrophiles in Methylene Chloride
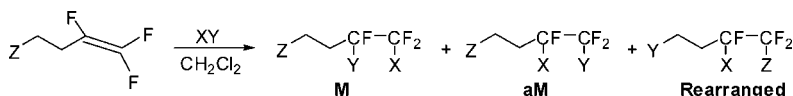
Run	Alkene (Z)	Electrophile XY	Dihalo Y = X	M	aM	Rearranged
1	1 (Cl)	Cl$_2$	8 100	...	...	...
2	1 (Cl)	Br$_2$	9 100	...	...	...
3	1 (Cl)	BrCl	56[a]	10 32	11 12	...
4	1 (Cl)	IBr	...	12 87	13 13	...
5	2 (Br)	Cl$_2$	14 98	...	...	12 2
6	2 (Br)	Br$_2$	15 100	...	...	...
7	2 (Br)	BrCl	29[b]	16 10[c]	17 14[c]	38[d] X = Z = Br; Y=Cl 9[d] X =Y= Cl; Z = Br
8	2 (Br)	ICl	...	18 36[e]	19 64[e]	...
9	2 (Br)	IBr	30[f]	20 4[g]	21 66[g]	...
10	3 (I)	Cl$_2$	22 75	...	...	23 25
11	3 (I)	Br$_2$	24 100[h]	...	...	...
12	3 (I)	IBr	41[i]	25 3[j]	26 54[j]	27 2

^{a} Chlorine and bromine in equilibrium with bromine monochloride in methylene chloride gave dichloro (**8**) and dibromo (**9**) in a ratio of 10:5.2, respectively. ^{b} Chlorine and bromine in equilibrium with bromine monochloride gave dichloro (**14**) and dibromo (**15**) in a ratio of 1.0:2.9, respectively. ^{c} Product ratio at 10−15 min reaction time as the ratios change at longer times. ^{d} Rearreanged products were 4-chloro-1,2-dibromo-1,1,2-trifluorobutane (**9**) in 38% and 1-bromo-2,4-dichloro-1,1,2-trifluorobutane (**10**) in 9%. ^{e} Product ratio obtained by extrapolating back to $t = 0$ since **18** rearranges to **19**. ^{f} Product **15** from equilibrium of bromine with iodine monobromine. ^{g} Product ratio obtained by extrapolating back to $t = 0$ since **20** rearranges to **21**. ^{h} Product **24** rearranges to **20** on standing. ^{i} Products from reaction of bromine in the 1.0 M IBr solution. They are **24** and **20** in a ratio of 1.0:1.4, respectively. ^{j} Product ratio extrapolated back to $t = 0$ since **25** rearranges to **26**.

chloronium ion from alkene **2**. Structure **A** was found to be the local minimum when calculations were started from structure **E**. Perhaps the small amount of rearranged product (2%; Table 3, run 5) represents a small contribution from **E** in methylene chloride as solvent. Bromine addition to **2** does not provide evidence for a five-membered-ring intermediate since migration of the 4-bromosubstituent cannot be discerned. Rearranged products are not observed for the reactions of ICl or IBr with alkene **2** (Table 3, runs 8 and 9).

In methylene chloride as solvent, the chlorination of **2** gives only a small amount of rearranged product (Table 3, run 5). However, Cl$_2$ and Br$_2$ from dissociation of BrCl gives **9** and 38% rearranged products, respectively (Table 3, run 7). The reaction of BrCl with alkene **2** is slow and requires about 15 min while the reactions of bromine or molecular chlorine are very fast. We suggest that Cl$_2$ and Br$_2$ in the presence of BrCl form a complex (Scheme 2).[9] A complex would account for the slow rate. Also, the resulting halonium cation and anion

SCHEME 2

$$2\ BrCl \rightleftharpoons Cl_2 + Br_2$$

$$X_2 + BrCl \rightleftharpoons [X_2 \cdot BrCl]$$

Complex

X = Cl or Br
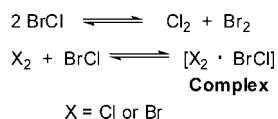
[XBrCl]⁻ pair may be longer lived and allow more time for rearrangement to the more stable five-membered-ring intermediate (Scheme 1, step k₃).

(3) Halonium Ions from 3. Reaction of Cl_2 with alkene **3** gives the most rearranged product (25%, Table 3, run 10). The open-chloronium ion **E** from alkene **3** is only 1.6 kcal/mol higher in energy than open-ion **A** (Table 2, run 7). We suspect that the rearranged product from chlorination of **3** is from intermediate **E** in equilibrium with **A**. The superb iodine neighboring group[10] accounts for the large amount of rearranged product. The three-membered-ring bromoniun and iodonium ions from alkene **3** are quite symmetrical (**C**⇒**D**, Table 1, runs 8 and 9), and no rearranged product is formed with Br_2 (Table 3, run 11). The 2% rearranged product from reaction of IBr with **3** probably results from the fact that iodine is a better leaving group than bromine in the three-membered-ring halonium ion.
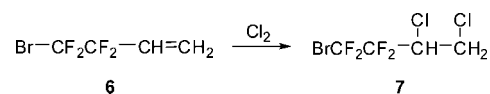
(4) Comparison of Halonium Ions from Alkenes 1, 2, and 3. Three-membered-ring halonium ions are formed better by iodine than bromine, and bromine bridges better than chlorine.[1] The open-ion structures **A** for the three chloronium ions from alkenes **1**, **2**, and **3** (Table 1, runs 1, 4, and 7) compared to the more symmetrical structures (**C**⇒**D**) for the bromonium and iodonium ions from these alkenes support our earlier observations[1] that iodine and bromine bridge better than chlorine. The similar calculated structures for the bromonium and iodonium ions are surprising.

Our calculations show that the structures of intermediates **A** and **C**⇒**D** are not dependent on the number-4 substituent. For example, structures of the open chloronium ions from alkenes **1**, **2**, and **3** are quite similar (Table 1, runs 1, 4, and 7), as are the bridged bromonium ions (Table 1, runs 2, 5, and 8) and the iodonium ions (Table 1, runs 3, 6, and 9). The similar structures calculated for the bromonium and iodonium ions are consistent with their nearly comparable product distributions from bromination (Table 3, runs 6 and 11) and iodination (Table 3, note the similar **aM/M** product ratios, runs 9 and 12). The small product differences from these three-membered bromonium vs iodonium ions cannot be predicted from calculations since their structures and charge density distributions are similar (Table 1, compare runs 2, 5, and 8 with runs 3, 6, and 9). The product differences can perhaps best be explained by the better leaving group ability of iodine vs bromine in the three-membered halonium ions (Table 3, compare runs 12 with 11). Also, better participation by the number-4 iodine compared to bromine may account for the small amount of rearranged product from the reaction of IBr with alkene **3** compared to **2** (Table 3, runs 12 and 9). Other factors that may influence the product distribution from similar calculated structures include the nature of the anion nucleophile in aprotic solvents (compare the **M/aM** ratio for reaction of ICl and IBr with alkene **2**, Table 3, runs 8 and 9).

The **M/aM** product ratio is greater for reaction of IBr than BrCl with alkene **1** (Table 3, runs 3 and 4) even though their calculated bromonium and iodonium ions structures are quite

similar (Table 1, runs 2 and 3) This effect may be due to the ring-opening difference of the bromine compared to the iodine in the three-membered halonium ions. Also there is more **M** product formed for reaction of ICl than with IBr for reactions with alkene **2** where identical iodonium ions are formed (Table 3, runs 8 and 9). Perhaps the smaller chloride anion in aprotic solvent can open the iodonium ion at the internal sterically hindered number-2 carbon better than the bromide anion (Table 3, runs 8 and 9).

(5) 4-Bromo-3,3,4,4-tetrafluorobut-1-ene (6). Chlorination of alkene **6** is very slow and did not give rearranged product. Ionic addition of Cl_2 to **6** is similar in reactivity to ionic reaction of Cl_2 with $1H,1H,2H$-perfluorooctene-1.[11] Experimental data in methanol indicated that the chloronium ion from $1H,1H,2H$-perfluorooctene-1 was rather symmetrical (**D**);[11] and calculations suggest a symmetrical intermediate (**C**) for the chloronium ion from 3,3,3-trifluoropropene.[2] Thus we expect the chloronium ion from **6** to be rather symmetrical and that it would not give rearranged product.

$$Br{-}CF_2CF_2{-}CH{=}CH_2 \xrightarrow{Cl_2} BrCF_2CF_2{-}\overset{\overset{\displaystyle Cl}{|}}{C}H{-}\overset{\overset{\displaystyle Cl}{|}}{C}H_2$$

6   **7**

B. Comparison of Intermediates from Addition of a Proton and Chlorine to Fluorosubstituted Terminal Alkenes. Acid-catalyzed addition of a proton to the hydrocarbon propene gives an open unbridged secondary carbocation intermediate. On the other hand, the chloronium ion from the chlorination of propene in the gas phase is bridged with a rather symmetrical structure **C** containing some small asymmetry approaching **B** (**C**⇒**B**).[2] Chlorination of alkenes like **1**, **2**, or **3** with three fluorine atoms results in an open-ion structure **A** as the lowest energy intermediate because the alkyl group and back-bond resonance from the single fluorine on carbon-2 gives a more stable intermediate than a bridged ion or a cation on the difluoroterminal carbon. This open-ion structure **A** is similar to that expected for addition of open-ion electrophiles like a proton (H⁺) to 1,1,2-trifluoroterminal alkenes. Our calculations show that a proton, like chlorine, also prefers to add to the terminal carbon of 1,1,2-trifluoropropene placing the positive charge on the number-2 carbon (Table 4, run 1). The energy difference between having the charge on the number-2 compared to the terminal carbon is small (1.3 kcal/mol). Thus one might expect both regioisomers to undergo addition of a proton to 1,1,2-trifluoroalkyl-1-enes with the preferred isomer having the added proton on the terminal carbon. Products from reaction of 70% perchloric acid with alkene **2** were not stable at the temperatures required.

Calculations show that the positive charge is greatly preferred on the number-2 carbon for addition of a proton to 1,2-difluoropropene and 2-fluoropropene (Table 4, runs 3 and 4). Hydration of 2-fluorooct-1-ene with perchloric acid/formic acid catalyst gave only 2-octanone. Similarly, reaction of 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bi (tetrafluoroborate) [F-TEDA-BF₄] with 2-fluorooct-1-ene in acetonitrile/water gave only 1-fluoro-2-octanone (see the Supporting Information). Earlier calculations predict an open-ion intermediate for chlorination of 2-fluoropropene,[2] and that was confirmed for chlorination of 2-fluorooct-1-ene in methanol where only

(9) Chiappe, C.; Del Moro, F.; Raugi, M. *Eur. J. Org. Chem.* **2001**, *18*, 3501.

(10) Peterson, P. E.; Bopp, R. J.; Chevli, D. E.; Curran, E. L.; Dillard, D. E.; Kamat, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 5902.

(11) Shellhamer, D. F.; Allen, J. L.; Allen, R. D.; Bostic, M. J.; Miller, E. A.; O'Neil, C. M.; Powers, B. J.; Price, E. A.; Probst, J. W.; Heasley, V.L. *J. Fluorine Chem.* **2000**, *106*, 103.

TABLE 4. Comparison of the Intermediates from Proton (H^+) and Chlorine (Cl_2) Addition to Fluorosubstituted Propenes[a]

Run	Alkene/Intermediate	Enthalpy(au)	ΔH^b (kcal/mole)	Lowest Energy Structure with Chlorine[c]
1	1,1,2-Trifluoropropene			
	$CH_3-CF-CF_2$ (H, ⊕)	−414.02716		
	$CH_3-CF-CF_2$ (⊕, H)	−414.02923	+1.3	$CH_3-CF-CF_2$ (⊕, Cl)
2	1,1-Difluoropropene			
	$CH_3-CH-CF_2$ (H, ⊕)	−315.16903	−18.3	$CH_3-CH-CF_2$ (Cl, ⊕)
	$CH_3-CH-CF_2$ (⊕, H)	−315.13987		
3	(E) 1,2-Difluoropropene			
	$CH_3-CF-CHF$ (H, ⊕)	−315.13655		
	$CH_3-CF-CHF$ (⊕, H)	−315.16619	+17.6	$CH_3-CF-CHF$ (⊕, Cl)
4	2-Fluoropropene	−216.24690		
	$CH_3-CF-CH_2$ (H, ⊕)			
	$CH_3-CF-CH_2$ (⊕, H)	−216.30587	+37.0	$CH_3-CF-CH_2$ (⊕, Cl)
5	1-Fluoropropene			
	$CH_3-CH-CHF$ (H, ⊕)	−216.27559	−2.5	
	$CH_3-CH-CHF$ (⊕, H)	−216.27240		CH_3-CH—CHF (bridged Cl, ⊕)

[a] Calculations were performed at the MP2 level using a 6−311+G** basis set on the Spartan 02 program. [b] A negative ΔH means the positive charge is more stable on carbon-1 than carbon-2. [c] Data from: Shellhamer, D. F.; Gleason, D. C.; Rodriguez, S. L.; Heasley, V. L.; Boatz, J. A; Lehman, J. J. *Tetrahedron*, **2006**, *62*, 11609.

1,2-dichloro-2-fluorooctane and the **M** product 1-chloro-2-fluoro-2-methoxyoctane was found.[1] The open-ion intermediate **A** for chlorination of 1,2-difluoropropene[2] is similar to that expected for addition of a proton (Table 4, run 3).

Calculations show that an open-ion with positive charge on the terminal carbon is also greatly preferred for addition of a proton or a chlorine[2] electrophile to 1,1-difluoropropene (Table 4, run 2). However, the positive charge is only slightly favored (2.5 kcal/mol) on the terminal carbon for protination of 1-fluoropropene (Table 4, run 5). Products were not stable to the reaction conditions for acid-catalyzed hydration of 1-fluorooct-1-ene. Our earlier calculations show that the intermediate for chlorination of 1-fluoropropene is bridged and rather symmetrical in the gas phase represented as **C⇒D**, but it is less symmetrical (**D⇒C**) when corrected for the solvent methanol.[2] Experimentally in methanol as solvent, the chloronium ion is highly unsymmetrical and may even be an open-ion since chlorination of (*E*)- or (*Z*)-1-fluorooct-1-ene gave only 1,2-dichloro-1-fluorooctane and the **aM** product 2-chloro-1-fluoro-1-methoxyoctane.[1] A bridged chloronium ion forms with 1-fluoro-1-alkenes because neither the terminal cation stabilized by back-bond resonance from the number-1 fluorine nor the number-2 secondary carbon cation are as stable as the bridged chloronium ion.

Conclusion

We have shown that five-membered-ring trifluorotetramethylene halonium ions (**5**) are indicated for reaction of some halogen electrophiles to alkenes **2** or **3** where the number-4 substituent is a bromine or iodine. The three strong electron-withdrawing vinyl fluorine atoms on alkenes **1**, **2**, and **3** attenuate the neighboring group effect since we did not find evidence for a neighboring group effect when the number-4 substituent is chlorine (alkene **1**). This is in contrast to the hydrocarbon where five-membered-ring tetramethylene chloronium ions are readily formed.[6–8] For halogen substituents on the number-4 carbon of 1,1,2-trifluoroterminal alkenes, iodine participates in neighboring group rearrangement better than bromine and the involvement of chlorine is not indicated. Quantum chemical calculations show that the chloronium ions from alkenes **1**, **2**, or **3** are unbridged and open-ions that form β-chlorocarbenium ions are similar to those reported by Ohta in super acid.[5] The increase in rearranged products is due to the increase in nucleophilicity of the number-4 halogen (Z) where I > Br > Cl. Bromonium and iodonium ions from these alkenes are rather symmetrical and similar in structure. The bromonium ions bridge well enough such that no rearranged products are found, except for the BrCl reaction where a complex changes the reaction. Experimental product distributions for bromination and iodination reactions with alkenes **2** or **3** cannot be predicted from their calculated structures because their intermediates are similar. Product distributions do correlate with structural differences of halonium ions when their calculated structures are different.[1,2]

The chloronium ions from terminal alkenes with vinyl fluorines tend to be open-ions[2] similar to the addition of a proton

except for the bridged chloronium ion from 1-fluoro-1-alkenes. A bridged chloronium ion from 1-fluoroterminal alkenes is rather symmetrical because the terminal fluorine and the alkyl group on the internal carbon each provide similar charge stabilization.[2]

Experimental Section

A. General Methods. Alkenes **1** and **3** were prepared from commercially available **2** in 37% and 83% yield, respectively. Alkene **1** was from reaction of dry lithium chloride with **2** in dry DMSO at 100 °C for 1 h in a pressure bottle. Alkene **3** (bp 117 °C at 760 Torr) was from reaction of **2** and potassium iodide with acetone as solvent at 90 °C for 4 h. Alkene **6** was commercially available. 2-Fluorooct-1-ene[12] and 1-fluorooct-1-ene[13] were synthesized from literature preparations.

Halogenation reactions were carried out as follows: Chlorine gas was slowly bubbled into a 1.0 M methylene chloride solution of alkene **1**, **2**, **3**, or **6** at room temperature and the progress followed by gas chromatography. For Br_2, ICl, or IBr, alkene **1**, **2**, or **3** (1.0 mmol) was added to 1.0 mmol of the halogen or interhalogen in 1.0 mL of methylene chloride at room temperature. Bromine monochloride (0.62 M in CH_2Cl_2) was prepared by adding an equivalent amount of Br_2 to a 0.62 M methylene chloride solution of Cl_2.

Product structural descriptions and ratios for reactions of halogen electrophiles with alkenes **1**, **2**, **3**, and **6** are given in Table 3. Reaction times and percent yields are in the Analytical section below. Most of the products were purified by preparative GC with a stainless steel 6 ft × $^3/_8$ in. column of 5% OV-17 on Chromosorb W 80/100. The remaining products were isolated by distillation from preparative scale reactions, or they were independently synthesized and/or converted by S_N2 reactions to known compounds.

Product **8** was compared to a commercial sample, and **16** is a known compound.[14,15] We characterized compounds **14**, **15**, **18**, and **19** earlier.[1] Products **7**, **9**, **12**, **13**, **17**, **21**, **22**, **23**, and **24** are characterized in the Supporting Information. Several reaction products were converted by S_N2 reaction of halide ion to replace the number-4 halogen converting it to a known compound. Thus compounds **10**, **11**, **22**, and **24** were converted by S_N2 reactions to known or characterized compounds **16**, **17**, **14**, and **15** (Supporting Information). Products **16**, **22**, and **24** were also independently synthesized, while **20**, **25**, **26**, and **27** decomposed during attempted purification and except for **26** they are minor products (Supporting Information).

B. Analytical Reactions. The following reactions of Cl_2 and Br_2 with alkene **1** are representative.

1,2,4-Trichloro-1,1,2-trifluorobutane (8). To a stirred solution of **1** (1.00 mmol) in 1.0 mL of methylene chloride at room temperature was slowly bubbled Cl_2 until all of the alkene was consumed. Product **8** was formed in 52% yield by GC analysis with pure **15** as internal standard. Spectral data for **8** were identical with those of a commercial sample.

1,2-Dibromo-4-chloro-1,1,2-trifluorobutane (9). To a stirred solution of 1.00 mmol of Br_2 in 1.0 mL of methylene chloride at room temperature was added 145 mg (1.00 mmol) of **1**. Product **9** was formed in 78% yield as determined by NMR analysis with benzene as internal standard. Product **9** is characterized in the Supporting Information.

Similarly (electrophile, alkene, time, percent yield) gave the following:

1,4-Dibromo-2-chloro- (10) and 2,4-Dibromo-1-chloro-1,1,2-trifluorobutane (11). BrCl, **1**, 20 min, 25 °C, 80% by GC with **15** as internal standard.

2-Bromo-4-chloro-1-iodo- (12) and 1-Bromo-4-chloro-2-iodo-1,1,2-trifluorobutanem (13). IBr, **1**, 12 h, 25 °C, 70% by NMR with benzene as internal standard.

4-Bromo-1,2-dichloro- (14) and 1,2,4-Tribromo-1,1,2-trifluorobutane (15). See preparative scale synthesis in the Supporting Information.

1,4-Dibromo-2-chloro- (16)[14,15] and 2,4-Dibromo-1-chloro-1,1,2-trifluorobutane (17). BrCl, **2**, 15 min., longer reaction times gave different product ratios due to thermodynamic rearrangement, 25 °C, 54% isolated yield by preparative GC.

4-Bromo-2-chloro-1-iodo- (18) and 4-Bromo-1-chloro-2-iodobutane (19). ICl, **2**, 15 min, the product ratio in Table 1 was obtained by extrapolating back to t = 0 due to equilibration, 25 °C, 74% by GC with **15** as internal standard. Compounds **18** and **19** were reported earlier.[1]

2,4-Dibromo-1-iodo- (20) and 1,4-Dibromo-2-iodo-1,1,2-trifluorobutane (21). IBr, **2**, 12 h, product ratios in Table 1 were obtained by extrapolating back to t = 0, 25°, 80% by GC with **15** as internal standard.

1,2-Dichloro-4-iodo- (22) and 2,4-Dichloro-1-iodo-1,1,2,-trifluorobutane (23). Cl_2, **3**, 15 min, 25 °C, 85% by GC with **14** as internal standard.

1,2-Dibromo-4-iodo-1,1,2-trifluorobutane (24). Br_2, **3**, 15 min, 25 °C, 95% by GC with **14** as internal standard.

2-Bromo-1,4-diiodo- (25), 1-Bromo-2,4-diiodo- (26), and 4-Bromo-1,2-diiodo-1,1,2-trifluorobutane (27). IBr, **3**, 12 h, product ratios in Table 1 were obtained by extrapolating back to t = 0, 50 °C, 72% by GC with **14** as internal standard.

C. Reactions with 2-Fluorooct-1-ene. See the Supporting Information.

D. Theoretical Methods. Geometry optimizations and vibrational frequency calculations were performed at the second-order perturbation theory level (MP2, also known as MBPT(2)),[16] using the GAMESS[17] quantum chemistry code. The 6-311++G(d,p) basis set[18] was used for all calculations. Harmonic vibrational frequencies were calculated for each structure to verify that the optimized structure is a local minimum on the ground-state potential energy surface. Löwdin atomic charges were obtained by using a Mulliken population analysis[19] based upon symmetrically orthogonalized orbitals.[20]

(16) (a) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. S10* **1976**, 1. (c) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *275*. (d) Bartlett, R. J.; Silver, D. M. *Int. J. Quantum Chem. Symp.* **1975**, *9*, 1927.

(17) (a) Gordon, M. S.; Schmidt, M. W., as cited in: Dykstra, C. E.; Frenking, G.; Kim, K. S.; Scuseria, G. E. *Theory and Applications of Computational Chemistry: The First Forty Years*; Elsevier: Amsterdam, The Netherlands, 2005. (b) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347–1363.

(18) (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (b) Blandeau, J.-P.; Davis, N. E.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 6104. (c) Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comp. Chem.* **1983**, *4*, 294.

(19) (a) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833–1840. (b) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1841–1846. (c) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 2338–2342. (d) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 2343–2346.

(20) Löwdin, P.-O. *Adv. Chem. Phys.* **1970**, *5*, 185–199.

(12) Eckes, L.; Hanack, M. *Synthesis* **1978**, 207.

(13) Cox, D. G.; Gurusamy, N.; Burton, D. J. *J. Am. Chem. Soc.* **1985**, *107*, 2811.

(14) Tarrant, P.; Gillam, E. G. *J. Am. Chem. Soc.* **1954**, *76*, 5423.

(15) Hinton, J. F.; Jaques, L.W. *J. Magn. Reson.* **1975**, *17*, 95.

Supporting Information Available: Procedures for independent synthesis of **16**, **22**, and **24** and preparative scale reactions to make **7**, **14**, and **15**, along with procedures to convert **24**, **22**, **10**, and **11** to **15**, **14**, **16**, and **17**, respectively, along with NMR (^{1}H, ^{19}F, ^{13}C) and GC/MS ([CH$_2$Z]$^{\bullet+}$, [CF$_2$X]$^{\bullet+}$, M$^+$, descriptive fragmentation and isotope cluster) data. This material is available free of charge via the Internet at http://pubs.acs.org.

JO800472E