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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.

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Reaction of Halogens and Interhalogens with 4-Halo-1,1,2-trifluorobut-1-enes: Rearrangement of 3-Membered Halonium to 5-Membered Trifluorotetramethylene Halonium Ion Intermediates and Comparison of Open-Chloronium Fluorosubstituted Ions to Fluorocarbocations from Protons (PREPRINT)

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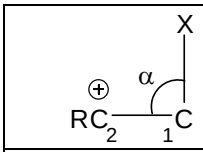
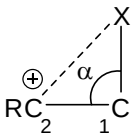
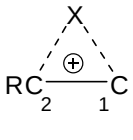
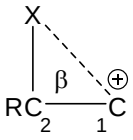
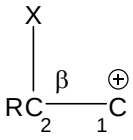
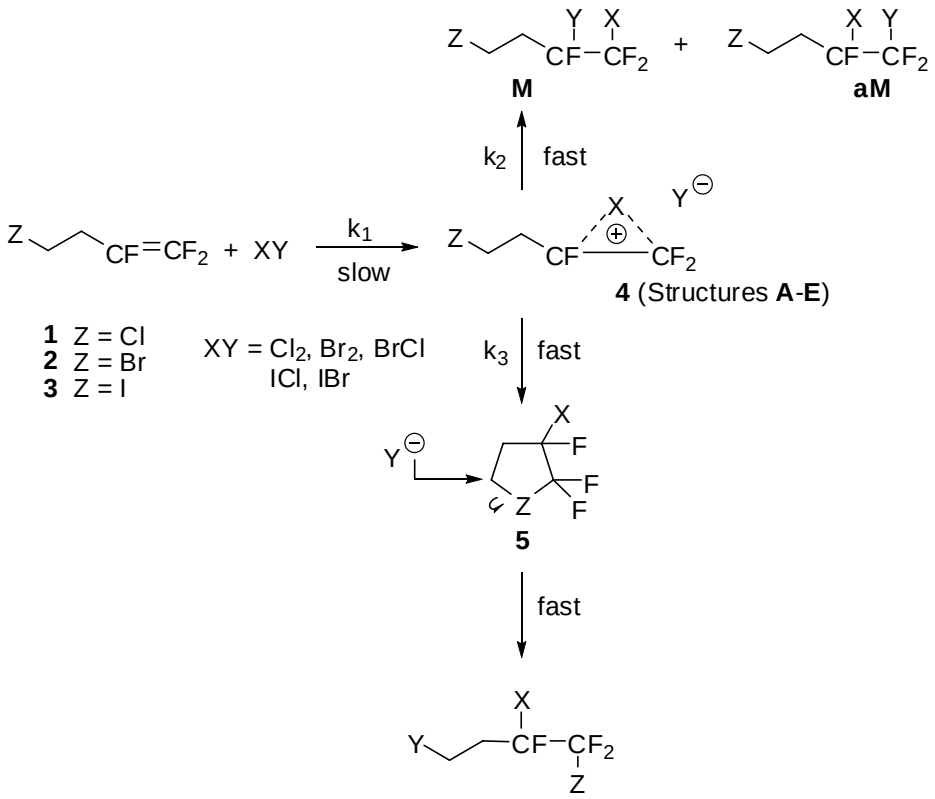
Introduction

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

				
A	**B**	**C**	**D**	**E**

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^o 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 bromonium ion **5** (Scheme 1, Z = Br).[1] The steric effect and repulsive forces from the lone-pair electrons

Scheme 1



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 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.

$ZCH_2CH_2CF{=}CF_2$

1 Z = Cl
2 Z = Br
3 Z = I

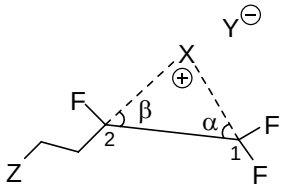
Results and Discussion

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

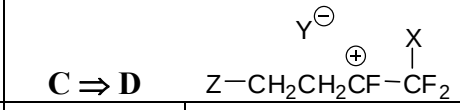
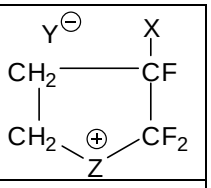
TABLE 1
HALONIUM ION BOND ANGLES (α, β) and CHARGE DENSITIES (C_1, C_2)



Run	Z	X	Y	BOND ANGLE		CHARGES		STRUCTURE BASED ON
				C_2–C_1–X(α)	X–C_2–C_1(β)	Q (C_2)	Q (C_1)	BOND 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**

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[5], in superacid media[6], and for the addition of trifluoroacetic acid to 5-chloro-1-hexene.[7] The five-membered trifluorochloronium ion **5** (Scheme 1, X=Y=Z=Cl) is 19.7 kcal more stable than the open-chloronium ion **A** (Table 2, run 1). Calculations also

TABLE 2
MP2/6-311++G(d,p) RELATIVE ENTHALPIES[a]
(ΔH_o, k cal/mole)

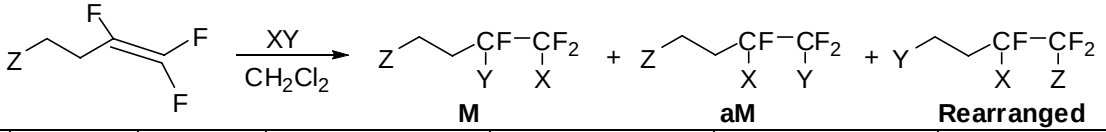
							
Run	**Z**	**X**	**Y**	**bridged (kcal/mole)**	**open-ion (kcal/mole) A**	**open-ion (kcal/mole) E**	**five-membered ring**
1	Cl	Cl	Cl		19.7[b]	21.1[b]	0
2	Cl	Br	Br	16.2			0
3	Cl	I	Br	11.6			0
4	Br	Cl	Cl		22.1	…[c]	0
5	Br	Br	Cl	18.6			0
6	Br	I	Cl	14.0			0
7	I	Cl	Cl		25.7[b]	27.3[b]	0
8	I	Br	Br	22.2		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

[a] Zero-point vibrational energy corrections scaled by 0.9748 (see A.P. Scott, L. Radom, *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**.

show that the open-chloronium ion **E** is only 1.4 kcal 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 percent 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.

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 minutes 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**

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 bromonium or iodonium ions even though the five-membered ring intermediates are more stable by 16.2 and 11.6 kcal, respectively (Table 2, runs 2 and 3).

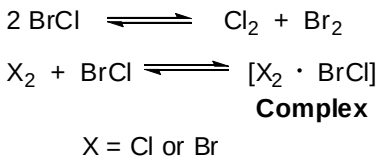
(2) *Halonium Ions from* **2**

Electrophilic addition of Cl_2 to alkene **2** gives 2 percent of rearranged product (Table 3, run 5). Intermediate **5** (Scheme 1, X=Y=Cl; Z=Br) is 22.1 kcal more stable than the open-ion **A** (Table 2, run 4). Our calculations did not find a local minimum **E** for an open-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 percent rearranged products, respectively (Table 3, run 7). The reaction of BrCl with alkene **2** is slow and requires about 15 minutes while the reactions of bromine or molecular chlorine are very fast. We suggest that Cl_2 and Br_2 in the presence of BrCl forms a complex (Scheme 2).[8] A complex would account for the slow rate. Also, the resulting halonium

cation and anion $[XBrCl]^-$ pair may be longer lived and allow more time for rearrangement to the more stable five-membered ring intermediate (Scheme 1, step k_3).

Scheme 2



(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 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[9] accounts for the large amount of rearranged product. The three-membered ring bromonium 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 percent 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.

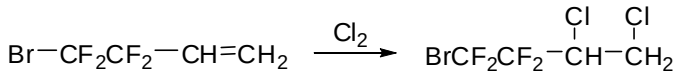
Our calculations show that the structures of intermediates **A** and **C⇒D** are not dependent on the number-4 substituent. For example, structures of the open chloronium ions from alkenes **1**, **2** and **3** are quite similar (Table 1, runs 1, 4 and 7), as are the bridged bromonium ions (Table 1, 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 2-3) 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.[10] Experimental data in methanol indicated that the chloronium ion from 1H,1H,2H-perfluorooctene-1 was rather symmetrical (**D**);[10] 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.



6 **7**

B. <u>Comparison of Intermediates from Addition of a Proton and Chlorine to Fluorosubstituted Terminal Alkenes.</u>

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 chlorination of propene 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

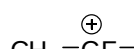
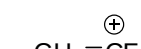
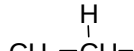
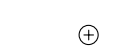
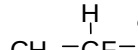
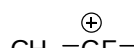
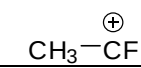
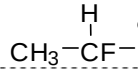
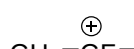
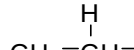
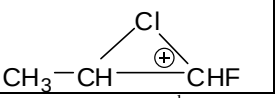
fluorine atoms results in an open-ion structure **A** as the lowest energy intermediate because the alkyl group and back-bond resonance from the single fluorine on carbon-2 gives a more stable intermediate than a bridged ion or a cation on the difluoroterminal carbon. This open-ion structure **A** is 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). Thus one might expect both regioisomers for 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 3and 4). Hydration of 2-fluorooct-1-ene with perchloric acid/formic acid catalyst gave only only 2-octanone. Similarly, reaction of 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis (tetrafluoroborate) [F-TEDA-BF_4] with 2-fluorooct-1-ene in acetonitrile/water gave only 1-fluoro-2-octanone (see 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 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) on the terminal carbon for protination of 1-fluoropropene (Table 4, run 5). Products were not stable

TABLE 4

COMPARISON OF THE INTERMEDIATES FROM PROTON (H^+) AND CHLORINE (Cl_2) ADDITION TO FLUOROSUBSTITUTED PROPENES[a]

Run	Alkene/Intermediate	Enthalpy(au)	Δ H[b] (kcal/mole)	Lowest Energy Structure with Chlorine[c]
1	1,1,2-Trifluoropropene 	–414.02716		
		–414.02923	+1.3	
2	1,1-Difluoropropene 	–315.16903	–18.3	
		–315.13987		
3	(E) 1,2-Difluoropropene 	–315.13655		
		–315.16619	+17.6	
4	2-Fluoropropene 	–216.24690		
		–216.30587	+37.0	
5	1-Fluoropropene 	–216.27559	–2.5	
		–216.27240		

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

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 a bridged and rather symmetrical structure 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.[5,6,7] 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. The

increase in rearranged products are 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

General Methods

Alkenes **1** and **3** were prepared from commercially available **2** in 37 and 83 percent yield, respectively. Alkene **1** was from reaction of dry lithium chloride with **2** in dry DMSO at 100 $^{\circ}$C for one hour in a pressure bottle. Alkene **3** (bp 117 ^{o}C at 760 Torr) was from reaction of **2** and potassium iodide with acetone as solvent at 90 ^{o}C for four hours. Alkene **6** was

commercially available. 2-Fluorooct-1-ene[11] and 1-fluorooct-1-ene[12] 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 mmole of the halogen or interhalogen in 1.0 mL 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 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'x 3/8" 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.[13,14] 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 Section).

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 Section).

Analytical Reactions

The 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 methylene chloride at room temperature was slowly bubbled Cl_2 until all of the alkene was consumed. Product **8** was formed in 52 percent yield by GC analysis with pure **15** as internal standard. Spectral data for **8** were identical to a commercial sample.

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

Similarly (Electrophile, alkene, time, percent yield) gave:

1,4-Dibromo-2-chloro-(**10**) and 2,4-Dibromo-1-chloro-1,1,2-trifluorobutane (**11**). (BrCl, **1**, 20 min., 25^o, 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-trifluorobutane(**13**). (IBr, **1**, 12 hours, 25°, 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 Section.

1,4-Dibromo-2-chloro-(**16**)[13,14] 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°, 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°, 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 hours. Product ratios in Table 1 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°, 85 % by GC with **14** as internal standard).

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

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

Reactions with 2-Fluorooct-1-ene. See Supporting Information Section..

Theoretical Methods

Geometry optimizations and vibrational frequency calculations were performed at the second-order perturbation theory level (MP2, also known as MBPT(2))[15], using the GAMESS[16] quantum chemistry code. The 6-311++G(d,p) basis set[17] 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 using a Mulliken population analysis[18] based upon symmetrically orthogonalized orbitals.[19]

Supporting Information Available

Procedures for independent synthesis of **16**, **22**, **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, are in the **Supporting Information** . NMR (^{1}H, ^{19}F, ^{13}C) and GC/MS ($[CH_2Z]^{+\cdot}$, $[CF_2X]^{+\cdot}$, M^+, descriptive fragmentation and isotope cluster) data are also given. This material is available free of charge via the Internet at http://pubs.acs.org.

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