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Symmetry of chloronium ions from ionic reaction of chlorine, chlorine monofluoride gas, and chlorine monofluoride complex with terminal alkenes

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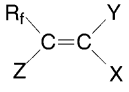
Abstract

Ionic chlorination of 1H,1H,7H-perfluorohept-1-ene (**2**) and heptafluoropropyl trifluorovinyl ether (**4**) with chlorine monofluoride (ClF) gas in aprotic solvent; and alkenes **2**, 1H-perfluorohept-1-ene (**3E**), and **4** with chlorine (Cl_2) in protic solvent were investigated. Regiochemical data from SN_2-like ring-opening of the intermediate was used to predict the symmetry of the chloronium ion. The chloronium ions from perfluorohydroalkene **2** with two terminal hydrogens were found to be unsymmetrical with positive charge localized on the terminal carbon. However, reaction of $ClF_{(g)}$ with **3E** containing a single terminal fluorine atom gave data suggesting a symmetrical chloronium ion. Alkene **4** contains a heptafluoropropyl ether group that stabilizes positive charge on the number-2 carbon and it is reactive enough to give products with the sluggish ClF complex generated in situ. Reactive eletrophiles $ClF_{(g)}$, $Cl_{2(g)}$, or the less reactive ClF complex, give an unsymmetrical chloromium ion with charge localized on the internal number-2 carbon.

Keywords: Chlorination; Protic solvent; Alkyl

1. Introduction

Recently, we demonstrated that the symmetry of halonium ions depends on the alkyl substituent and the number and position of vinyl hydrogens replaced with a fluorine [1,2]. We also demonstrated that iodonium ions form a tighter bridged species than bromine, and that bromine bridges better than chlorine. Chlorine (Cl_2) is a stronger electrophile than bromine or iodine and can better react with electron-deficient alkenes [3]. In this paper, we report on the reaction of Cl_2 in methanol with the electron-deficient alkene 1H-perfluorohept-1-ene (**3E**) and chlorine monofluoride gas ($ClF_{(g)}$) with 1H,1H,7H-perfluorohept-1-ene (**2**). In the formation of products, alkene **3E** provides stereochemistry capable of detecting a competing free-radical process. Furthermore, both stereo-and regiochemistry data can be obtained from the solvent incorporated chloromethoxy products from chlorination of **3E** in methanol.



1	$R_f = nC_5F_{11}$	X=Y=Z=F
2	$R_f = HCF_2(CF_2)_4$	X=Y=H; Z=F
3E	$R_f = nC_5F_{11}$	X=H; Y=Z=F
4	$R_f = nC_3F_7O$	X=Y=Z=F
5	$R_f = R_H = nC_4H_9$	Z=Y=Z=H

We also compared product regiochemistry from reactions with the more reactive alkenes **4** and **5** (Table 1). Alkenes **4** and **5** are able to participate in electrophilic reactions with the sluggish electrophile ClF generated in situ and also with the very reactive $ClF_{(g)}$ molecule. We have demonstrated in an earlier paper that ClF generated from *N*-chlorosuccinimide or alkyl hypochlorites and a source of hydrogenfluoride such as xenon difluoride or triethylamine trihydrofluoride [$(C_2H_5)_3N{\cdot}3HF$] were sluggish electrophiles and therefore could not involve a free $ClF_{(g)}$ molecule [4]. We concluded that ClF generated from these reagents deliver the elements of Cl and F from a "complexed ClF" [4].

2. Results and discussion

Perfluoroheptene-1 (**1**) is unreactive and requires 2 weeks to consume ca. 10% alkene for the ionic chlorination (Cl_2) of

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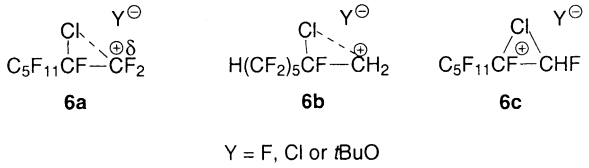
Table 1
Addition of chlorine and chlorine monofluoride to terminal alkenes

Reagent	Solvent[a]	Alkene	R, A, B, D	M: Y (%)	aM: Y (%)	Ratio **M/aM**
$ClF_{(g)}$[b]	CH_2Cl_2	**1**	nC_5F_{11}–, F, F, F	F (0)	F (100)	**aM** only
Cl_2[b,c]	*t*-BuOH	**1**	nC_5F_{11}–, F, F, F	*t*-BuO (0)	*t*-BuO (100)	**aM** only
$ClF_{(g)}$[d]	CH_2Cl_2	**2**	$H(CF_2)_5$–, F, H, H	F (6)	F (94)	0.06
Cl_2[d]	*t*-BuOH	**2**	$H(CF_2)_5$–, F, H, H	*t*-BuO (0)	*t*-BuO (100)	**aM** only
Cl_2[d,e]	CH_3OH	**3E**	nC_5F_{11}–, F, H, F	CH_3O (65)	CH_3O (35)	1.8
$ClF_{(g)}$[d]	$CHCl_3$	**4**	nC_3F_7O–, F, F, F	F (86)	F (14)	6.1
t-BuOCl[d]/$(C_2H_5)_3N{\cdot}3HF$	CH_2ClCH_2Cl	**4**	nC_3F_7O–, F, F, F	F (70)	F (30)	2.3
Cl_2[f]	CH_3OH	**4**	nC_3F_7O–, F, F, F	CH_3O (71)	CH_3O (29)	2.4
t-BuOCl[g]/$(C_2H_5)_3N{\cdot}3HF$	CH_2Cl_2	**5**	nC_4H_9, H, H, H	F (87)	F (13)	6.7
Cl_2[h]	CH_3OH	**5**	nC_4H_9–, H, H, H	CH_3O (73)	CH_3O (27)	2.7

[a] Reactions ran at 25 °C, except **5** in methanol was run at 0 °C.
[b] [3].
[c] Ratio of 1,2-dichloro-to **aM** product was 96:4.
[d] This work.
[e] Ratio of dichloro to chloromethoxy products 5.7:1. *Erythro* products from **3E**.
[f] [1].
[g] [4].
[h] [12].

1 in protic solvent [3]. Ionic reaction of $ClF_{(g)}$ with **1** in aprotic solvent required only 2 h [3]. Replacing the vinyl fluorines with hydrogens makes the alkenes (**2** and **3E**) more reactive. For example, ionic chlorination of **3E** in protic solvent required only 2 days (Section 3). Data for reaction of unreactive alkenes **1**, **2** and **3E** with Cl_2, and **1** and **2** with $ClF_{(g)}$ are in Table 1. Only *anti*-Markovnikov (**aM**) products were found for reaction of Cl_2 and $ClF_{(g)}$



with alkene **1** and these data are consistent for an unsymmetrical intermediate **6a** [1,3,4]. The small amount of Markovnikov (**M**) product for reaction of $ClF_{(g)}$ with **2** in methylene chloride suggest that **6b** has more charge on carbon-2 than **6a**. The absence of any **M** product for reaction of Cl_2 with **2** in *tert*-butanol may represent dispersal of charge from carbon-2 by the protic solvent, or it may be that the ''naked'' fluoride ion in methylene chloride is a superb nucleophile capable of SN_2-like attack at carbon-2. The smaller amount **aM** product (35%) for chlorination of **3E** compared to exclusive **aM** product from **1** and **2** represents too great a difference to be explained by the solvent effect between methanol and *tert*-butyl alcohol. We suggest that the two terminal fluorines of **1** stabilize charge on the terminal carbon better than the single fluorine on **3E**. Fluorine is known to stabilize positive charge on an α-carbon by back-bond resonance and to inductively destabilize positive charge on a β-carbon [5].

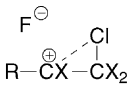
The terminal carbon of **6c** contains only a single fluorine to stabilize the positive charge through back-bond resonance on carbon-1 and inductively destabilize positive charge on the β-carbon-2.

Reaction of Cl_2 with alkenes **1** or **2** in *tert*-butyl alcohol gave only **aM** solvent incorporated products in low yield (5–10%, Table 1); the major components were the 1,2-dichloroproducts.[2] Although oxygen is a very effective free-radical inhibitor for chlorination reactions, the energy of an ionic transition state may be raised significantly for electron-deficient alkenes such as **1**–**4**, allowing a free-radical process to intervene via initiation by molecule-induced homolysis [6,7]. We treated 1H-perfluorohept-1-ene (**3E**) with Cl_2 in methanol, and the confirmation of an ionic pathway in this case is that *erythro* products are formed. The ratio **M/aM** of 1.8 is in the range of a symmetrical intermediate such as **6c** as defined in our earlier paper [1].

Alkenes **4** and **5** are sufficiently electron-rich and, therefore, react with the ''complexed ClF'' electrophile generated from *t*-BuOCl/$(C_2H_5)_3N{\cdot}3HF$. The large amount of **M** products for reaction of $ClF_{(g)}$ or ''complexed ClF'' (generated in situ) with alkenes **4** and **5** are consistent with unsymmetrical intermediates **7a**, and **b**. Unsymmetrical chloronium

[2] *tert*-Butyl alcohol rather than methanol was used as solvent for these very slow reactions since chlorine slowly oxidized methanol.

ions like **7a**, and **b** are indicated when the **M/aM** product ratio is greater than 2:1 (Table 1) [1]. These unsymmetrical chloronium ions **7a**, and **b** in aprotic solvents are similar to the chloronium ions from alkenes **4** and **5** with Cl_2 in methanol [1].



7a R = nC_3F_7O ; X = F

7b R = nC_4H_9 ; X = H

Data in Table 1 show that more **M** product is formed for reaction of alkene **4** with $ClF_{(g)}$ than from the "complexed ClF." This observation lends more support to our earlier claim that a free $ClF_{(g)}$ molecule is not formed when generated in situ from *N*-chlorosuccinimide or alkylhypochlorites and a source of hydrogen fluoride [4]. It is clear from these studies that synthetically $ClF_{(g)}$ is required for reactions with electron-deficient substrates. However, reagents like alkyl hypohalites or *N*-halosuccinimides and a source of hydrogen fluoride that produce the "complexed ClF" can be used to deliver the elements of chlorine and fluorine to alkenes and aromatics that are electron-rich [4,8,9].

3. Experimental

3.1. General procedures and instrumentation

Chemicals were purchased from Syn Quest Inc., except for $ClF_{(g)}$ which was from PCR chemicals and *t*-BuOCl from TCI. Alkene **2** was prepared as described in [10]. Instruments used were described in our earlier work [3].

3.1.1. Reaction of chlorine monofluoride with 2

Caution: $ClF_{(g)}$ is dangerous. Consult a qualified person for assistance.

To 148 mg (0.50 mmol) **2**, 50 mg perfluorooctyl bromide as internal standard, and 1.6 ml dry methylene chloride in a dry flash under nitrogen purge was slowly bubbled ClF/N_2. The reaction progress was followed by GC and terminated after 75% of the alkene reacted. Products (Table 1) were formed in 60% yield by GC analysis based on the alkene consumed. The **aM** 1H,1H,7H-2-chlorododecafluoroheptane was obtained pure by preparative GC on a 3.0 m × 1.6 cm. stainless steel column with 5% Carbowax 20 M on 80/100 Chromosorb W. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 4.80$ (ddd, $J = 45.9$, 14.4 and 11.6 Hz, 1H), 4.85 (ddd, $J = 45.9$, 17.3 and 11.6 Hz, 1H), 6.06 (tt, $J = 51.9$ and 4.9 Hz, 1H). ^{19}F (282 MHz, $CDCl_3$) $\delta = -118.1$ (AB pattern, 2F), −120.7 (AB pattern, 2F), −123.7 (m, 2F), −129.9 (m, 2F), −134.5 (m, 1F), −137.5 (m, 2F), −224.5 (m, 1F). MS. EI (70 eV) *m/z* (rel. intensity) $M^+ - [CHF_2, ClF]$ 245 (16); 131 (18); 113 (21); $[CH_2FCFCl]^+$ 101, 99 (45, 100); $[CF_2H]^+$ 51 (50); $[CH_2F]^+$ 33 (15). PCI (CH_4) $M + 1 - [HF]$ 333, 331 (32, 100). HRMS EI $M^+ - [F]$ calcd. for $C_7H_3ClF_{11}$ 330.9748; found: 330.9743. IR (gas) 3020 (w), 2970 (w), 1204 (s), 1137 (m), 946 (w), 760 (w) and 732 (w) cm^{-1}. The **M** minor regioisomer was independently synthesized [10] and has the identical GC/MS to our compound. EI $[CF_2CH_2Cl]^+$ 101, 99 (40, 100); 69 (26), $[CF_2H$ and $CH_2Cl]^+$ 51, 49 (42, 12).

3.1.2. Reaction of chlorine monofluoride with 4

Reaction with **4** was carried out as above except chloroform was used as solvent as methylene chloride has a GC retention time equal to one of the products. Products (Table 1) were obtained in 80% yield by GC analysis with perfluorooctyl bromide as internal standard. Products were isolated from reaction of $ClF_{(g)}$ with 2.66 g neat **4** followed by preparative GC with a 3.0 m × 0.64 cm in stainless steel column of 20% OV-210 on 80/100 Chromosorb W-HP. **M** product 1-chloro-3-oxoperfluorohexane. ^{19}F NMR (282 MHz, $CDCl_3$) $\delta = -71.2$ (AB pattern, 2F); −77.3 (m, 2F); −81.6 (t, $J = 8$ Hz, 3F); −84.5 (dm, $J = 146$ Hz, 1F); −86.3 (dm, $J = 146$ Hz, 1F); −130.4 (m, 2F). MS. EI (70 eV) $M^+ - 19$, 303, 301 (1, 4); $M^+ - 69$, 253, 251 (3, 9); $[CF_3CF_2CF_2]^+$ 169 (99); 151 (49); $[CF_3CF_2]^+$ 119 (27); 101 (27); 100 (45); $[CF_2Cl]^+$ 87, 85 (31, 82); $[CF_3]^+$ 69 (100); $[CF_2]^+$ 50 (41); $[Cl]^+$ 37, 35 (4, 14). **aM** regioisomer 2-chloro-3-oxoperfluorohexane. ^{19}F NMR (282 MHz, $CDCl_3$) $\delta = -13.4$ (m, 1F); −77.2 (m, 2F); −81.6 (t, $J = 8$ Hz, 3F); −86.1 (m, 3F); −130.2 (m, 2F). MS. EI (70 eV) $M^+ - [CF_3]$ 253, 251 (8, 25); $[CF_3CF_2CF_2]^+$ 169 (98); $[CF_3CF_2]^+$ 119 (29); 103 (60); 101 (88); 100 (45); $[CF_3]^+$ 69 (100); $[CF_2]^+$ 50 (27); $[Cl]^+$ 37, 35 (6, 19). HRMS EI on mixture of both **M** and **aM** regioisomers calcd. for $M^+ - [F]$ $C_5F_{10}OCl$ 300.9478; found: 300.9478.

3.1.3. Reaction of tert-butyl hypochlorite and triethylamine trihydrogenfluoride with 4

The reaction was carried out as described in our earlier paper [4] in ethylene dichloride since methylene chloride has a GC retention time that interferes with products. Products (Table 1) were obtained in ca. 30% yield by GC analysis with perfluorooctyl bromide as internal standard. Products were confirmed by comparison of their GC/MS data to the isolated products above.

3.1.4. Ionic reaction of chlorine with alkene 2

In a dry 5 ml flask with Teflon stopper was added 2.4 ml *t*-BuOH, 60 mg perfluorooctyl bromide as internal standard, 148 mg (0.50 mmol) alkene **2** and 8 mg mercuric acetate as catalyst. A drying tube replaced the Teflon stopper and the mixture cooled in an ice bath. Oxygen was slowly bubbled through the cooled mixture followed by chlorine until saturation. The Teflon stopper was secured to the flask and the contents stirred in the dark at room temperature for 2 weeks. Oxygen and chlorine were again introduced as above. GC analysis after a total reaction time of 4 weeks showed that more than 10% of alkene **2** had reacted. The

1,2-dichloro- and **aM** 1-*t*-butoxy-2-chloro-products were found in a 99:1 ratio, respectively. The 1,2-dichloroprodcut was prepared by photochemical reaction of Cl_2 with **2** and characterized earlier [1]. Attempted independent synthesis of the **aM** product, 1H,1H,7H-1-*t*-butoxy-2-chloroundecafluoroheptane by photochemical reaction of *t*-butylhypochlorite with **2** gave a complex mixture of products. The structure of this minor product is based on its GC/MS data. EI *m/z* (rel. intensity) $[t\text{-BuOCH}_2]^+$ 87 (4); $[t\text{-BuO}]^+$ 73 (1); $[t\text{-C}_4\text{H}_9]^+$ 57 (100); $[\text{HCF}_2]^+$ 51 (5); $[\text{C}_3\text{H}_5]^+$ 41 (52).

3.1.5. Ionic reaction of chlorine with alkene *3E*

Alkene **3E** was prepared using Burons procedure [11]. The reaction of Cl_2 with **3E** was carried out as above for alkene **2** except anhydrous methanol was used. GC analysis showed that 35% of **3E** reacted after 2 days in the dark at room temperature with the products given in Table 1. The dichloro-product 1H-1,2-dichloroperfluoroheptane was found to be an *erythro/threo* mixture of 98:2; the *threo*-isomer from a possible competing free-radical pathway. The dichloroproduct was isolated from photochemical chlorination (300 W sunlamp) of 0.5 mmol **3E**, reaction progress followed by GC (*erythro/threo* ratio 54:46), in 65% yield by NMR integration with 1,2-dichlorobenzene as internal standard. Preparative GC on the OV-210 column above gave 1H-1,2-dichloroperfluoroheptane in 99% purity by GC analysis from which the following data were obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ = *threo* 6.47 (dd, J = 48.3 and 9.3 Hz), *erythro* 6.61 (d, J = 48.1 Hz). ^{19}F (282, $CDCl_3$) $\delta = -81.2$ (t, J = 11 Hz, 3F), −116.0 (AB pattern, 2F), −119.7 (AB pattern, 2F), −123.0 (m, 2F), −126.5 (m, 2F), [*erythro/threo* −129.8 (m) and −134.5 (m), 1F], [*erythro/threo* −144.5 (m) and −145.5 (m), 1F]. GC/MS of *erythro* identical to *threo*. EI M^+ − Cl 369, 367 (0.2, 0.5); $[CF_3\text{-}CF_2CF_2]^+$ 169 (4); $[CF_3CF_2]^+$ 119 (16); $[CF_2Cl]$ 87, 85 (5, 16); $[CF_3$ and $CHFCl]^+$ 69, 67 (100, 96). PCI (CH_4) reporting ^{35}Cl only $M+1$ − [HF] 383 (90); $M+1$ − [HCl] 367 (100). HRMS PCI (CH_4) $M+1$ − [HF] calcd. for $C_7H_1Cl_2F_{12}$ 382.9264; found: 382.9280. IR (gas) on *erythro/threo* 54:46 mixture: 3009 (w), 1357 (w), 1243 (s), 1150 (m), 1025 (w) and 710 (w) cm^{-1}.

3.1.6. Independent synthesis of 1H-2-chloro-1-methoxy perfluoroheptane

The *erythro*-**aM** product 1H-2-chloro-1-methoxy perfluoroheptane had identical GC/MS data to that prepared by independent synthesis from photochemical (300 W sunlamp) reaction of methyl hypochlorite[3] to **3E** using the procedure to prepare to other **aM** products [1,7]. *erythro/threo*-Isomers were formed in equal amounts. The following data were obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ = [3.70 (s) and 3.74 (s), 3H], 5.52 (dm, J = 63 Hz, 1H). ^{19}F (282 MHz, $CDCl_3$) $\delta = -81.2$ (t, J = 10.7 Hz, 3F), −117.8 (m, 2F), −120.5 (m, 2F), −123.1 (m, 2F), −126.5 (m, 2F), [−134.5 (m) and −136.1 (m), 1F], [−135.4 (dd) and −140.3 (dd), J = 63 and 17 Hz, 1F]. GC/MS of *erythro* identical to *threo*. EI M^+ − Cl 381, 379 (2, 7); 169 (8); 131 (9); 119 (7); 69 (40); $[CHF{=}O^+CH_3]$ 63 (100). PCI (CH_4) $M+1$ 399 (50); $M+1$ − [HF] 379 (100). HRMS CI (CH_4) $M+1$ − [HF] calcd. for $C_8H_4ClF_{12}O$ 378.9759; found 378.9764. IR (gas) on mixture: 3024 (w), 2950 (w), 2866 (w), 1345 (w), 1240 (s), 1142 (m), 1015 (w), 1031 (w) and 750 (w) cm^{-1}.

Attempted synthesis of the **M** product, 1H-1-chloro-2-methoxy perfluoroheptane by ionic chlorination with various metal catalysts was unsuccessful. The structure of this minor product is based on its GC/MS. EI (70 eV) M^+ − $[CF_3CF_2]$ 281, 279 (11, 34); M^+ − $[C_6F_6]$ 262, 260 (10, 24); M^+ − $[CF_3CF_2;\ OCH_3;\ Cl]$ 213 (34); $[CH_3OCFCHFCl]^+$ 131, 129 (3, 9); [CHFCl and $CF_3]^+$ 69, 67 (75, 100).

Acknowledgements

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References

[1] D.F. Shellhamer, J.L. Allen, R.D. Allen, D.C. Gleason, C. O'Neill Schlosser, B.J. Powers, J.W. Probst, M.C. Rhodes, A.J. Ryan, P.K. Titterington, G.G. Vaughan, V.L. Heasley, J. Org. Chem. 68 (2003) 3932.
[2] D.F. Shellhamer, D.C. Gleason, G.G. Vaughan, A.J. Ryan, P.K. Titterington, V.L. Heasley, J.J. Lehman, J. Fluorine Chem. 123 (2003) 173–176.
[3] D.F. Shellhamer, J.L. Allen, R.D. Allen, M.J. Bostic, E.A. Miller, C.M. O'Neill, B.J. Powers, E.A. Price, J.W. Probst, V.L. Heasley, J. Flourine Chem. 106 (2000) 103.
[4] D.F. Shellhamer, M.J. Horney, B.J. Pettus, T.L. Pettus, J.M. Stringer, V.L. Heasley, R.G. Syvrey, J.M. Dobrolsky Jr., J. Org. Chem. 64 (1999) 1094.
[5] C.G. Krespan, V.A. Petrov, Chem. Rev. 96 (1996) 3269.
[6] D.F. Shellhamer, V.L. Heasley, J.E. Foster, J.K. Luttrull, G.E. Heasley, J. Org. Chem. 42 (1977) 2141.
[7] D.F. Shellhamer, V.L. Heasley, J.E. Foster, J.K. Luttrull, G.E. Heasley, J. Org. Chem. 43 (1978) 2652.
[8] D.F. Shellhamer, B.C. Jones, B.J. Pettus, T.L. Pettus, J.M. Stringer, V.L. Heasley, J. Fluorine Chem. 88 (1998) 37.
[9] D.F. Shellhamer, M.J. Horney, A.L. Toth, V.L. Heasley, Tetrahedron Lett. 33 (1992) 6903.
[10] Y. Zaperalov, L.V. Saloutine, M.I. Kodess, I.P. Kolenko, Zh. Org. Khimii. 24 (1988) 1626 (Engl. Trans. 1466).
[11] C.R. Davis, D.J. Buron, J. Org. Chem. 62 (1997) 9217.
[12] van Ch. Duschek, M. Hampel, W. Pritzkow, J. Prakt. Chem. 317 (1975) 335.

[3] See [4] above and references therein.