*Journal of Fluorine Chemistry*, 65 (1993) 223–226

# Electrophilic reactions of 2-chloroperfluoro-1,3-butadiene

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## Abstract

Electrophilic chlorofluorination and bromofluorination of 2-chloroperfluoro-1,3-butadiene (**1**) have been found to occur exclusively at the 1,4-positions and regioselectively. Under mild conditions, diene **1** interacts with $SbF_5$ to form vinyl derivatives of antimony.

## Introduction

The ionic addition of some electrophilic reagents to fluoro-containing 1,3-dienes giving principally *trans*-1,4-adducts have been reported previously [1]. In electrophilic addition reactions involving 2-chloroperfluoro-1,3-butadiene (**1**), the absence of regioselectivity might be expected because an initial attack of the electrophile is basically possible both at the trifluorovinyl and at the difluorochlorovinyl fragments of the molecule of diene **1**. In addition, diene **1** is a vinylog of trifluorochloroethene, which is known to react ambiguously with most electrophilic reagents [2].

## Results and discussion

It has been found that electrophilic bromofluorination (*N*-bromosuccinimide in anhydrous HF) and chlorofluorination (hexachloromethylamine in anhydrous HF) of diene **1** proceed exclusively at the 1,4-positions and regioselectively with the initial attack of the electrophile being directed only at the difluoromethylene fragment of the trifluorovinyl group in the starting diene (Scheme 1).

The results obtained can be explained as follows (Scheme 2). When the electrophile attacks the $CF_2{=}CF$ group of the initial diene **1**, the relatively stable allyl cation A is formed which contains a chlorine atom in the 2-position of the allylic triad.

The other possible direction of attack should result in the formation of allyl cation B containing a fluorine atom in the 2-position and a chlorine atom in position 1 of the allylic triad. The only difference between these cations is the relative position of the fluorine and chlorine atoms (1,2- or 2,1-, see Scheme 2) in the allyl system. It is known [3] that the presence of the chlorine and fluorine at position 2 and 1, respectively, confers a greater stability on the fluorine-containing allyl cation, and hence cation A must be more stable in comparison with cation B. This fact determines the direction of the electrophilic attack.

The charge is distributed at positions 1 and 3 in the allyl cation; hence stabilization of the unsymmetrical cation A by addition of a fluoride anion from the medium can occur both in position 1 as well as position 3. However, the only product of the reaction is the internal olefin which is formed as a result of the addition of fluoride anion at position 3 of the allyl system.

Such selectivity arising from the stabilization of cation A may be connected with the substantial asymmetry in the distribution of positive charge or with steric hindrance arising from fluoride anion attack at position 1.

Diene **1** did not react with anhydrous HF over the temperature range 20–150 °C. A further increase in temperature (to 200 °C) leads to the well-known thermal cyclization of **1** with the formation of perfluorochlorocyclobutene [4]. Attempts to conduct the reactions of diene **1** with acids stronger than HF (trifluoromethanesulphonic and fluorosulphonic acids) also failed. Nevertheless, diene **1** reacts with $SbF_5$ under mild conditions in $SO_2ClF$ to form a mixture of antimony(V) vinyl derivatives (Scheme 3).

In our opinion, the formation of compounds **4** and **5** is connected with a preliminary isomerization of diene **1** into 1-trifluoromethyl-1-chloroperfluoroallene (**6**) (under the action of $SbF_5$) which, in turn, undergoes attack by the electrophilic particle $SbF_4^+$ at its central carbon atom to give the corresponding allyl cation C. Stabi-

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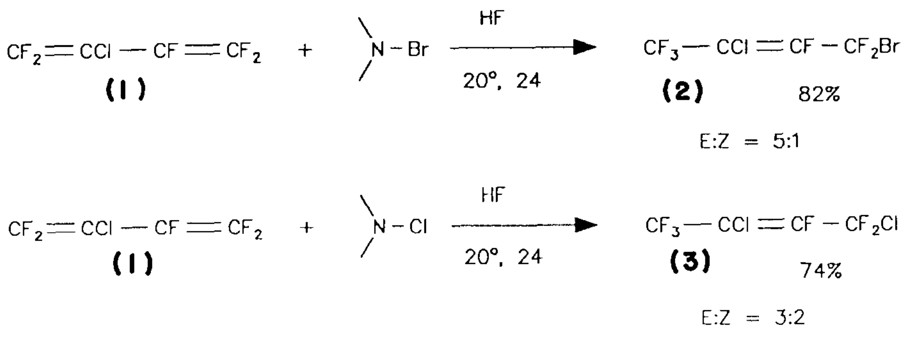
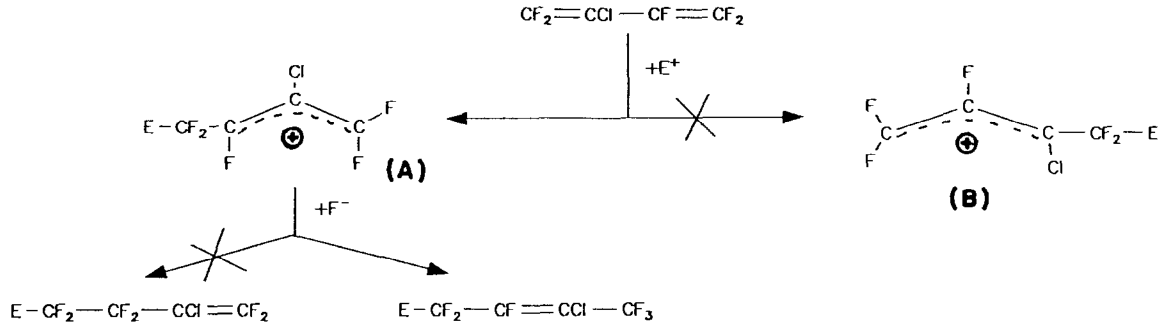
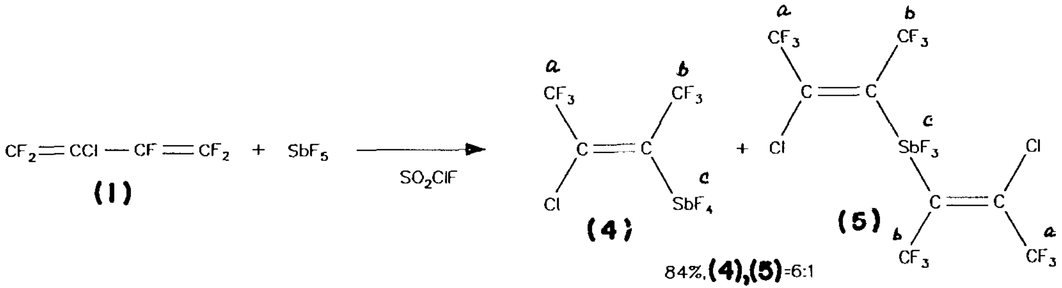


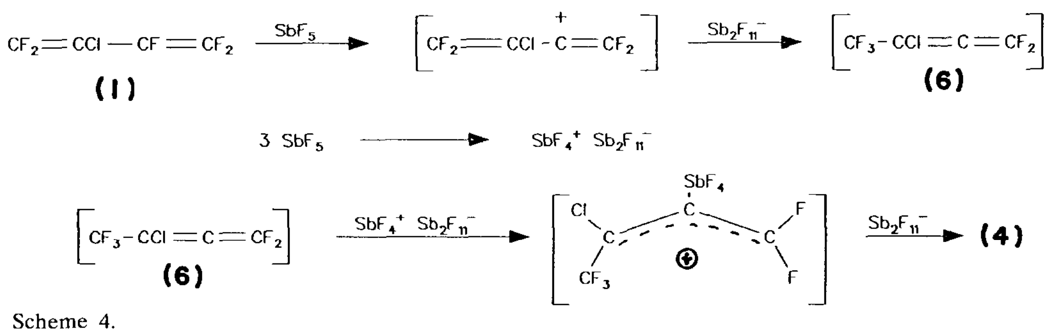
Scheme 1.



Scheme 2.



Scheme 3.



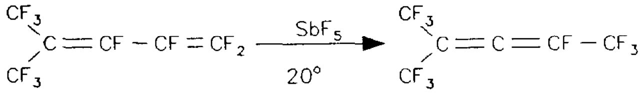
Scheme 4.

lization of cation C results in the final reaction product **4**. Product **5** is formed in a similar manner (Scheme 4).

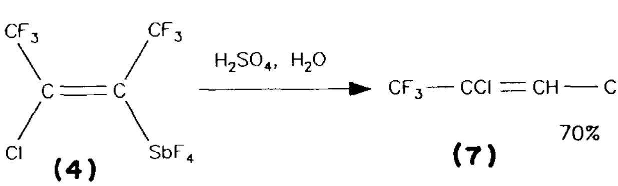
The possibility of such an isomerization of a perfluorodiene into an allene has been reported previously [5] in, for example, 2-trifluoromethylperfluoro-2,4-pentadiene which isomerizes into the corresponding allene under the action of $SbF_5$ in mild conditions (Scheme 5).

It is also known [6, 7] that perfluorinated allenes readily add electrophilic reagents (HF, $BF_3$) with initial attack by the electrophile being directed at a central carbon atom of the allene system; this may be attributed to the formation of a relatively stable allyl cation in this case.

On heating a mixture of compounds **4** and **5**, the former readily enters into a protodemetallation reaction



Scheme 5.



Scheme 6.

with 70% $H_2SO_4$ to form 2-chloro-3-hydroperfluorobut-2-ene (7) (Scheme 6).

## Experimental

NMR spectra were obtained using a Bruker WP-200 SY instrument [$^{19}F$ (188.3 MHz) and $^{13}C$ (50.3 MHz)]. Chemical shifts are quoted relative to TMS and $CF_3COOH$. Mass spectra were registered with a VG 7070E instrument. Raman spectra were recorded on a Ramanor HG-2S spectrometer with $Ar^+$ laser agitation (using the band at 514.5 nm). Diene **1** was obtained according to ref. 8.

### *Preparation of 2-chloro-4-bromoperfluorobut-2-ene (2)*

*N*-Bromosuccinimide (10.0 g, 0.055 mol), 75 ml anhydrous HF and diene **1** (10.26 g, 0.057 mol) were placed in a steel autoclave. The autoclave was allowed to stand for 24 h at 20 °C with stirring and then excess HF was distilled from the autoclave through a gas washing bottle filled with water. The reaction mixture was poured into ice, the lower layer separated, dried over $CaCl_2$ and distilled. Product **2** (7.0 g, 82%) was obtained, b.p. 81.5–82 °C. According to $^{19}F$ NMR analysis, this is a mixture of *E*- and *Z*-isomers in a 1:5 ratio.

$\overset{c}{C}F_3–CCl=\overset{b}{C}F–\overset{a}{C}F_2Br$: $^{19}F$ NMR $\delta$: *Z*-isomer: $-23.10$ ($2F^a$); $-12.76$ ($3F^c$); 24.4 ($F^b$) [$J$(a–b) = 17 Hz, $J$(b–c) = 16 Hz] ppm. *E*-isomer: $-23.30$ ($2F^a$); $-12.76$ ($3F^c$); 32.12 ($F^b$) [$J$(a–b) = 10.3 Hz, $J$(b–c) = 26.4 Hz] ppm. Raman ($\nu$, $cm^{-1}$): 1674 (C=C). MS: 278 $M^+$ (0.9); 258.93 $[M-F]^+$ (4.0); 197.03 $[M-Br]^+$ (100); 208.99 $[M-CF_3]^+$ (7.4); 149.11 $[M-CF_2Br]^+$ (24.7); 131 $C_3F_5{}^+$ (3.0); 131 $CF_2Br^+$ (1.6); 109.12 $C_3F_2Cl^+$ (13.9); 93.11 $C_3F_3{}^+$ (47.9); 69 $CF_3{}^+$ (45.2).

### *Preparation of 2,4-dichloroperfluorobut-2-ene (3)*

Diene **1** (10.0 g, 0.056 mol), hexachloromethylamine (6.00 g, 0.018 mol) and 75 ml anhydrous HF were placed into a steel autoclave. The autoclave was allowed to stand for 24 h at 20 °C with stirring, then excess HF was distilled from the autoclave through a gas washing bottle filled with water. The reaction mixture was poured into ice, the lower layer separated, dried over $CaCl_2$ and distilled. Product **3** (9.61 g, 74%) was obtained, b.p. 64–65 °C. According to $^{19}F$ NMR data, this is a mixture of *E*-and *Z*-isomers in a 1.5:1 ratio.

$\overset{c}{C}F_3–CCl=\overset{b}{C}F–\overset{a}{C}F_2Cl$: $^{19}F$ NMR $\delta$: *Z*-isomer: $-21.5$ ($2F^a$); $-18.2$ ($3F^c$); 24.6 ($F^b$) [$J$(a–b) = 12 Hz, $J$(a–c) = 15 Hz, $J$(b–c) = 10 Hz] ppm. *E*-isomer: $-20.9$ ($2F^a$); $-13.1$ ($3F^c$); 32.3 ($F^b$) [$J$(a–b) = 9 Hz, $J$(b–c) = 10 Hz] ppm. $\overset{4}{C}F_3–\overset{3}{C}Cl=\overset{2}{C}F–\overset{1}{C}F_2Cl$: $^{13}C$ NMR $\delta$: *E*-isomer: 119.2 ($C^1$); 155.3 ($C^2$); 112.9 ($C^3$); 119.9 ($C^4$) $^1J(C^1–F) = 290$ Hz, $^2J(C^4–F) = 37.5$ Hz, $^1J(C^3–F) = 271$ Hz, $^1J(C^4–F) = 272$ Hz] ppm. *Z*-isomer: 119.0 ($C^1$); 149.6 ($C^2$); 112.9 ($C^3$); 119.6 ($C^4$); [$^1J(C^1–F) = 290$ Hz, $^2J(C^4–F) = 32.5$ Hz, $^1J(C^3–F) = 285$ Hz, $^1J(C^4–F) = 272$ Hz] ppm. Raman ($\nu$, $cm^{-1}$): 1674 (C=C). MS: 232 $M^+$ (18.0); 213 $[M-F]^+$ (8.5); 197 $[M-Cl]^+$ (92.7); 163 $[M-CF_3]^+$ (37.6); 147 $[M-CF_2Cl]^+$ (100); 109 $C_3F_2Cl^+$ (18.5); 93 $C_3F_3{}^+$ (56.3); 85 $CF_2Cl^+$ (17.4); 69 $CF_3{}^+$ (65.2). Analysis: Found: C, 20.72; F, 49.07; Cl, 30.21%. $C_4F_6Cl_2$ requires: C, 20.60; F, 48.93; Cl, 30.47%.

### *Preparation of (1-trifluoromethyl-2-chloro-trifluoroprop-1-enyl)antimony tetrafluoride (4) and bis(1-trifluoromethyl-2-chloro-trifluoroprop-1-enyl)antimony trifluoride (5)*

A mixture consisting of 6.00 g (0.034 mol) diene **1** and 10 ml $SO_2ClF$ was introduced into a two-necked flask fitted with a reflux condenser and cooled with solid $CO_2$ at $-10$ °C, and then 7.4 g (0.034 mol) $SbF_5$ was added dropwise with vigorous stirring. A mixture (13.2 g, m.p. 126 °C, b.p. 145 °C/1mmHg) was obtained containing 84% **4** and 16% bis(1-trifluoromethyl-2-chlorotrifluoroprop-1-enyl)antimony trifluoride (**5**). According to $^{19}F$ NMR data, **4** and **5** exist as a mixture in a 6:1 ratio.

*cis*-$C\overset{a}{F}_3CCl=C(C\overset{b}{F}_3)Sb\overset{c}{F}_4$: $^{19}F$ NMR $\delta$: $-27.8$ ($3F^b$); $-14.3$ ($3F^a$); 32.5 (broad multiplet, $F^c$) [$J$(a–b) = 24 Hz] ppm.

*cis*-$[C\overset{a}{F}_3CCl=CC\overset{b}{F}_3]_2Sb\overset{c}{F}_3$: $^{19}F$ NMR $\delta$: $-28.2$ ($3F^b$); $-14.6$ ($3F^a$); 38.5 (broad multiplet, $F^c$) [$J$(a–b) = 24 Hz] ppm. IR ($\nu$, $cm^{-1}$): 1604 (C=C). MS of **4**+**5** mixture [$M_1$ = **4**; $M_2$ = **5**]: 555 $[M_2-F]^+$ (18.0); 393 $[M_2-C_4F_7]^+$ (43.1); 377 $[M_1-F]^+$ (54.0); 355 $[M_2-C_4F_9]^+$ (4.9); 337 $[C_4F_7ClSb]^+$ (2.6); 231 $[SbF_2Cl_2]^+$ (2.2); 215 $[SbF_3C]^+$ (7.6); 198 $[C_4F_6Cl]^+$ (4.0); 180 $[C_4F_5Cl]^+$ (17.6); 177 $[C_4F_6]^+$ (20.5); 177 $[SbFCl]^+$ (20.5); 162 $[C_4F_6]^+$ (13.7); 143 $[C_4F_5]^+$ (100); 109 $[C_3F_2C]^+$ (84.9); 85 $[CF_2Cl]^+$ (5.4).

### *Preparation of 2-chloro-3-hydrohexafluorobut-2-ene (7)*

The mixture (3.50 g) of **4**+**5** was dissolved in 6 ml of 70% $H_2SO_4$ with heating and the volatile product formed distilled off. Product **7** (1.1 g, 71%) was obtained, b.p. 34–35 °C (lit. value [8] 34.5–35.5 °C). According to $^{19}F$ NMR data, product **7** exists as a mixture of *E*- and *Z*-isomers in a 2:1 ratio.

$\overset{a}{C}F_3{-}CCl{=}CH{-}\overset{b}{C}F_3$: $^{19}F$ NMR $\delta$: *E*-isomer: $-18.6$ ($3F^a$); $-11.3$ ($3F^b$) [$J$(a–b) = 20 Hz] ppm. *Z*-isomer: $-15.2$ ($3F^a$); $-5.3$ ($3F^b$) ppm.

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