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New hydrofluorocarbon (HFC) solvents for antimony pentafluoride Generation and characterization of 1-alkoxypentafluoroallyl cations

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ABSTRACT

Certain hydrofluorocarbons (HFC) stable towards the strong Lewis acid, antimony pentafluoride, were found to function as a solvent for this aggressive reagent. $CF_3CF_2CH_2F$ (HFC-236cb) was demonstrated to be an excellent solvent for SbF_5 and was used for the generation of stable polyfluorinated benzyl and allyl cations. Using this solvent 1-methoxypentafluoroallyl cation and $R_FOCF{=}CFCF_2^+$ (R_F = *n*-C_3F_7 and *n*-C_4F_9), were generated and characterized by NMR spectroscopy.

1. Introduction

Rapid development in the area of carbocation chemistry began after the pioneering work of Olah, who utilized the strong Lewis acid—antimony pentafluoride [1–4]. Due to a unique combination of high Lewis acidity, affinity to halogens, a relatively wide liquid range (bp 153 °C, mp 8 °C) [5] its ability to enhance the acidity of protic acids and the commercial availability, SbF_5 quickly became the Lewis acid of choice for the generation of inorganic and carbon-based cations [3,6].

Despite of all these benefits, the high viscosity, relatively high melting point and pronounced oxidative properties of pure SbF_5 makes this material difficult to handle, especially at low temperature. To alleviate this problem, antimony pentafluoride is usually used in solution. The most common solvents for experiments involving SbF_5 are $HOSO_2F$, HF, SO_2 and SO_2ClF.

There are two general ways to generate carbocations in solution. The first approach is based on the protonation by the mildly electrophilic H^+ [7] of a nucleophilic functional group (–OH, C=O, C=C, etc.) of the organic substrate. Antimony pentafluoride is usually added into the corresponding acid such as HF, $HOSO_2F$, or CF_3SO_3H to increase the acidity of the Bronsted acid [6].

The second approach is based on the abstraction of a halide ligand by SbF_5 and requires aprotic conditions. These processes are usually carried out in solvents such as SO_2 or SO_2ClF. It should mentioned, that in contrast to SO_2ClF, which weakly interacts with SbF_5 [8,9], sulfur dioxide forms a stable solid complex, significantly reducing the Lewis acidity of SbF_5 and it can be used as a solvent only in a limited number of reactions. Sulfur dioxide also is able to undergo reactions with highly electrophilic cations [10–14].

Discovered in 1936, sulfuryl chlorofluoride (SO_2ClF) [15] was employed as a solvent for generation of positively charged species by Olah and Gillespie [16–20]. Due to its high dielectric constant, low nucleophilicity, wide liquid range (bp 7.1 °C, mp −124.7 °C), and high chemical stability towards electrophilic reagents, SO_2ClF became the solvent of choice for reactions involving strong oxidizers and Lewis acids, especially SbF_5 [3,6]. On the other hand, sulfuryl chlorofluoride is relatively expensive and its synthesis involves additional purification step due to the presence of sulfur dioxide in crude SO_2ClF [21].

Despite their great stability towards strong oxidizing agents and Lewis acids, perfluorocarbons are poor solvents for SbF_5. Perfluorocyclobutane is the only known exception. It was used successfully as a solvent for the generation of perfluoro- allyl and methallyl cations [7,22]). However, the relatively high melting point (−41 °C) precludes the use of perfluorocyclobutane in low temperature experiments.

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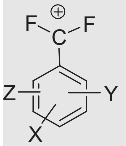
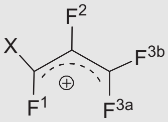
Table 1
NMR data of polyfluorinated benzyl and allyl cations in HFC's solvents





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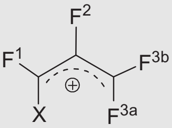


b

Entry no.	Cation	^{19}F NMR[a]	^{1}H NMR[a]	^{19}F NMR, reported values (δ, ppm, J, Hz) [reference]
1	**2a** X = 4-F, Y, Z = H	5.9 (2F, d, $J = 20.7$), −41.3 (1F, tm, $J_{t} = 20.7$)	8.2 (1H, d), 8.8 (1H, d), 9.8 (1H, s)	5.9 (d, 20.1), −45.0 [24]
2	**2b** X = 2-F, Y, Z = H	21.1 (1F, dd, $J = 244, 125$), 13.9 (1F, tm, $J = 244, 30$), −65.8 (1F, ddm, $J = 125, 30, 5$)	7.6 (1H, t), 7.9 (1H, t), 8.6 (1H, m), 8.9 (1H, m)	20.9 (1F, dd, $J = 246, 118$), 13.5 (1F, tm, $J = 246, 38$), −69.2 (1F, dd, $J = 118, 38$) [27]
3	**2c** X = 3-CF_3, Y, Z = H	23.2 (1F, d, $J = 264$), 22.5 (1F, d, $J = 264$), −65.1 (3F, s)	8.3 (1H, t, $J = 8$), 9.0 (1H, d, $J = 8$), 9.10 (1H, d, $J = 8$), 9.13 (1H, s)	
4	**2d** X = 4-CF_3, Y, Z = H	26.6 (2F, s) −66.3 (3F, s)	8.3 (1H, d, $J = 8$), 9.2 (1H, d, $J = 8$)	
5	**3**	22.7 (1F, dd, $J = 71, 10$), −63.4 (3F, d, $J = 12$), −71.7 (1F, br s, $\Delta\nu_{1/2} = 40$ Hz), −127.8 (1F, q, $J = 12$)	7.6 (t), 7.8 (t), 8.2 (t), 8.50, 8.7, 8.8[b]	
6	**5a** X = 2-F, Y = 6-Br, Z = H	25.4 (1F, dd, $J = 258, 131$), 19.1 (1F, dd, $J = 258, 34$), −65.7 (1F, ddm, $J = 258, 131$)	7.7 (1H, t, $J = 9.3$), 8.7 (1H, s), 9.0 (1H, m)	
7	**5b** X = Y = 3,4-Cl, Z = H	25.4 (1F, d, $J = 240$), 11.0 (1F, d, $J = 240$)	8.2 (1H, dd, $J = 8, 2$), 8.7 (1H, d, $J = 9$), 8.8 (1H, m, $J = 1.3$)	
8	**5c** X = Y = Z = 2,4,6-F	19.2 (2F, m), −29.03 (1F, m), −66.9 (2F, m)[c]	8.1 (m)	
9	**5d** X = 3-Br, Y = 5-CF_3, Z = H	26.03 (1F, d, $J = 277$), 25.45 (1F,d, $J = 277$), −67.44 (3F, s)	8.79 (2H, br s), 8.93 (1H, br s)	
10	**5e** X = Y = 3,5-CF_3, Z = H	33.37 (2F, br s), −64.85 (6F, br s)[d]	9.2 (br s), 9.35 (br s)[d,e]	36.9; −65.2 [24]
11	**7a** (X = C_6F_5)	−0.1 (1F^{3b}, dd,), −12.17 (1F^{3a}, dm), −20.5 (1F^{1}, m), −107.46 (2F, br s), −111.52 (1F, br s), −137.50 (2F, m), −164.0 (1F^{2}, m), $J_{3a-3b} = 209$, $J_{2-3a} = 92$, $J_{1-3b} = 40$		2.1 (1F^{3b}, m), −9.8 (1F^{3a}), −21.6 (1F^{1},) −109.2 (2F), −113.2 (1F), −137.5 (2F), −164.1 (1F^{2}, m), $J_{1-2} = 112$, $J_{1-3a} = 159$, $J_{1-3b} = 40$, $J_{2-3a} = 94$, $J_{3a-3b} = 209$ [28]
12	**8a**[a,c] (X = F)	22.50 (2$F^{a,a'}$, m), 2.53 (2$F^{b,b'}$, m), −183.92 (1F^{2}, t, $J = 100$)[c]		23.50 (2F, m), 3.7 (2F, m), −187.9 (1F, t, $J = 100$) [29]
13	**10a**[d,f] (X = OCH_3)	0.31 (1F^{1}, ddd), −31.72 (1F^{3b}, ddd), −49.25 (1F^{3a}, ddd), −189.35 (1F^{2}, ddd), $J_{1-2} = 69$, $J_{1-3a} = 115$, $J_{1-3b} = 17$, $J_{2-3a} = 110$, $J_{3a-3b} = 102$		
14	**10b**[d,f] (X = OCH_3)	17.78 (1F^{1}, dt), −31.00 (1F^{3a}, ddd), −47.10 (1F^{3b}, td), −190.52 (1F^{2}, ddd), $J_{1-2} = 15$, $J_{1-3a} = 13$, $J_{1-3b} = 68$, $J_{2-3a} = 111$, $J_{2-3b} = 25$, $J_{3a-3b} = 108$		
15	**10a**[h,i] (X = OCH_3)	−1.3 (1F^{1}, ddd), −34.3 (1F^{3b}, ddd), −52.0 (1F^{3a}, ddd), −191.3 (1F^{2}, ddd), $J_{1-2} = 69$, $J_{1-3a} = 115$, $J_{1-3b} = 17$, $J_{2-3a} = 110$, $J_{3a-3b} = 102$	4.62 (br s)	−74.2 (2F), −73.7 (1F), −76.4 (1F) [30][j]
16	**10b**[h,i] (X = OCH_3)	18.0 (1F^{1}, dt), −31.5 (1F^{3b}, ddd), −48.9 (1F^{3a}, td), −192.6 (1F^{2}, ddd), $J_{1-2} = 15$, $J_{1-3a} = 13$, $J_{1-3b} = 67$, $J_{2-3a} = 111$, $J_{2-3b} = 25$, $J_{3a-3b} = 107$	4.63 (t, $J = 2.4$)	
17	**11a** (X = Cl)			24.6 (1F^{1}), 1.9 (1F^{3a}), −10.8 (1F^{3b}), −163.3 (1F^{2}), $J_{1-2} = 118$, $J_{1-3a} = 156$, $J_{1-3b} = 40$, $J_{2-3a} = 96$, $J_{3a-3b} = 232$ [31][h]
18	**11b** (X = Cl)			56.4 (1F^{1}), −0.6 (1F^{3a}), −17.5 (1F^{3b}), −154.9 (1F^{2}), $J_{1-2} = 14$, $J_{1-3a} = 32$, $J_{1-3b} = 104$, $J_{2-3a} = 96$, $J_{3a-3b} = 232$ [31][h]

Table 1 (*Continued*)

19	**12a**[d,k] (X = n-OC$_3$F$_7$)	0.70 (1F^{3b}, d), −5.53 (1F^1, ddm), −18.67 (1F^{3a}, ddd), −74.96 (2F) −127.53 (2F) −80.86 (3F) −183.42 (1F^2, dd) J_{1-2} = 91, J_{1-3a} = 137, J_{2-3a} = 104, J_{3a-3b} = 187
20	**12b**[d,k] (X = n-OC$_3$F$_7$)	15.18 (1F^1, d), 0.46 (1F^{3b}, dm), −16.28 (1F^{3a}, dd), −74.51 (2F) −127.35 (2F) −80.86 (3F) −185.10 (1F^2, d) J_{1-3b} = 92, J_{2-3a} = 97, J_{3a-3b} = 182
21	**13a**[d,l] (X = n-OC$_4$F$_9$)	0.50 (1F^{3b}, d), −5.52 (1F^1, ddm), −18.77 (1F^{3a}, ddd), −73.83 (2F), −80.92 (3F, m, J = 10), −123.76 (2F), −125.9 (2F), −183.48 (1F^2, dd) J_{1-2} = 92, J_{1-3a} = 137, J_{2-3a} = 101, J_{3a-3b} = 181
22	**13b**[d,l] (X = n-OC$_4$F$_9$)	15.17 (1F^1, d), 0.25 (1F^{3b}, dm), −16.50 (1F^{3a}, dd), −73.39 (2F, m), −80.98 (3F, m, J = 10), −123.55 (2F, m), −125.9 (2F, m), −185.10 (1F^2, dm), J_{1-3b} = 92, J_{2-3a} = 106, J_{3a-3b} = 182

[a] δ, ppm; J, Hz; relative to signals of HFC-236cb: −84.52 ppm (**CF$_3$**), −127.58 (**CF$_2$**), −243.63 (CH$_2$**F**) ppm (^{19}F) and 4.64 ppm (**CH$_2$**F, ^{1}H) relative to external CFCl$_3$ and TMS reference, respectively); spectra acquired at 25 °C (for cations **8** at −50 °C; **12a** and **13a** at −20 °C).

[b] Partial overlap with signals of cation **2b**.

[c] Higher order NMR spectrum.

[d] In equilibrium with starting material.

[e] Partial overlap of two signals.

[f] In HFC-236cb solvent.

[g] ^{19}F NMR data for p-CH$_3$O–C$_6$H$_4$CF═CF–CF$_2^+$(in SO$_2$, CFCl$_3$, external): −53.1 (1F, J = 59, 22 Hz), −64.8 (1F, 105.5, 97.5, 59), −68.6 (1F, 105.5, 70.5, 3 Hz), −180.6 (97.5, 70.5, 22 Hz) [30].

[h] In SO$_2$ClF solvent.

[i] ^{13}C ({H}, SO$_2$ClF, C$_6$H$_6$ external, mixture of isomers): 71.7 (d, J = 7.8 Hz), 71.9 (m), 119.2 (2 signals, dm, J_d = 243 Hz), 165.20 (td, J = 332.3, 36.0), 172.70 (ddd, J = 360.4, 23.3, 16.5 Hz), 173.3 (dm, J = 354 Hz) ppm.

[j] In SO$_2$ solvent (CFCl$_3$, external).

[k] Ratio **12a**:**12b**, 63:37.

[l] Ratio **13a**:**13b**, 64:36.

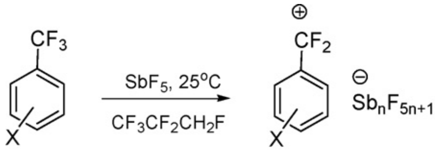
Recently, a simple, practical and scalable process for the preparation of hydrofluorocarbons (HFC's) involving condensation reaction of CH$_2$F$_2$ or CH$_3$F with tetrafluoroethylene and hexafluoropropene was reported [23]. The reaction is catalyzed by SbF$_5$ and produces the corresponding hydrofluorocarbons in 67–95% yield. During the scale up of the synthesis of CF$_3$CF$_2$CH$_2$F (HFC-236cb; bp 0–1 °C) it was noticed that antimony pentafluoride has a relatively high solubility in liquid HFC-236cb. These observations prompted us to attempt the use of HFC-236cb as a solvent for antimony pentafluoride.

2. Results and discussions

In sharp contrast to perfluoroalkanes, antimony pentafluoride has surprisingly high solubility in HFC-236cb. For NMR studies, the solutions containing up to 60 mol% of SbF$_5$ in HFC-236cb were prepared routinely. Concentrated solutions of SbF$_5$ in C$_2$F$_5$CH$_2$F can be cooled to −78 °C for short periods of time (10–15 min) without precipitation of SbF$_5$, allowing the addition of sensitive substrates and the acquisition of NMR spectra at low temperatures.

The difference between solutions of SbF$_5$ in SO$_2$ClF and HFC-236cb are evident in ^{19}F NMR spectra acquired near ambient temperature. In SO$_2$ClF solution at 15 °C, the ^{19}F nuclei of SbF$_5$ are in rapid exchange, and are observed as one, very broad (1200 Hz) resonance at −113 ppm (similar ^{19}F NMR spectrum of the solution SbF$_5$ in SO$_2$ClF at room temperature was previously reported by Dean and Gillespie [8]). By contrast, in HFC-236cb solution, at ambient temperature three broad, but distinct ^{19}F resonances of SbF$_5$ in ratio 1:2:2 are observed at −81.8, −102.2, −131.0 ppm, which implies the lack of fluoride abstraction from HFC-236cb by the SbF$_5$, but rather self-aggregation of SbF$_5$ [8].

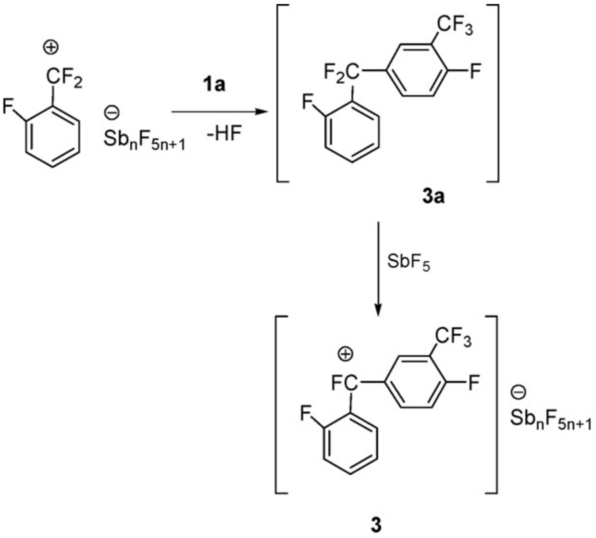
The addition of the corresponding benzotrifluorides **1a–d** to the solution of SbF$_5$ in HFC-236cb results in the formation of stable benzyl cations **2a–d**, respectively.



1a, X=4-F **2a**
1b, X=2-F **2b**
1c, X=3-CF$_3$ **2c**
1d, X=4-CF$_3$ **2d**

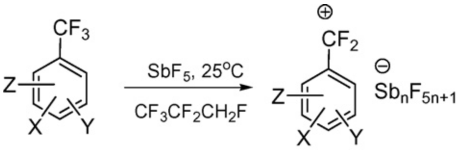
The ^{19}F NMR spectra of fluorinated cations **2a–d** exhibit a set of signals in the region 0 to +30 ppm. Observed values of chemical shifts and coupling constants of known cations **2a**, **2b** and **2d** are in good agreement with data reported previously [24–26] (see Table 1, entries 1–4).

In case of non-symmetrical cations **2b** and **2c**, the signals of two fluorine substituents bound to the carbon bearing positive charge appear as an AB multiplet with geminal coupling constants $^2J_{FF}$ = 244 and 264 Hz, respectively, typically observed in polyfluorinated benzyl cations. [32] All four cations prepared in HFC-236cb solvent were found to be stable at ambient temperature. Since approximately threefold molar excess of SbF$_5$ was used in all experiments, the signals of starting benzotrifluorides were absent in the NMR spectra, indicating high stability of the corresponding carbocations. In the ^{19}F NMR spectrum of **2b** an additional set of signals was present. It was assigned to the cation **3** (ratio **2b**:**3**, 5:1) This product forms as the result of electrophilic attack of **2b** on the starting material, followed by fluoride anion abstraction from CF_2 group of **3a** by SbF_5.



It should be pointed out that both chemical shifts for fluorine substituents bound to charged carbon and the coupling constant with the *ortho*- fluorine substituent in cation **3** are in good agreement with values reported for similar fluorinated systems obtained through electrophilic condensation of fluorinated benzyl cation with starting benzotrifluoride [33,34].

Treatment of polyfluorinated benzotrifluorides **4a**–**e** bearing two or three electron withdrawing substituents by SbF_5 in HFC-236cb results in the formation of stable cations **5a**–**e**.



4a	X=2-F, Y=6-Br, Z=H	**5a**
4b	X=Y=3,4-Cl, Z=H	**5b**
4c	X=Y=Z= 2,4,6-F	**5c**
4d	X=3-Br, Y=5-CF_3, Z=H	**5d**
4e	X=Y=3,5-CF_3, Z=H	**5e**

The reaction is clean and the formation of byproducts was not observed, despite the fact that the NMR spectra were acquired at ambient temperature. Fluorine resonances of the cations **5a**–**c** are sharp and well resolved. However, in the case of the cations **5d**,**e** signals in the NMR spectra are broadened, due to the exchange between carbocation and the starting arene, indicating lower stability of **5d**,**e** compared to **5a**–**c**. Parameters of ^{19}F and ^{1}H NMR spectra of **5e** are in a good agreement with reported values [24] (see Table 1). Other HFC's can be also used as solvents for generation of carbocations. For example cations **5a** and **5b** were generated in $(CF_3)_2CFCH_2F$ (HFC-338mmy) solvent. However, SbF_5 has noticeably lower solubility in this hydrofluorocarbon, which limits use of HFC-338mmy as solvent due to rapid precipitation of SbF_5 at subambient temperatures.

The addition of tetrafluorodithietane **6** to the solution in HFC-236cb with excess of SbF_5 results in immediate precipitation of insoluble white solid.

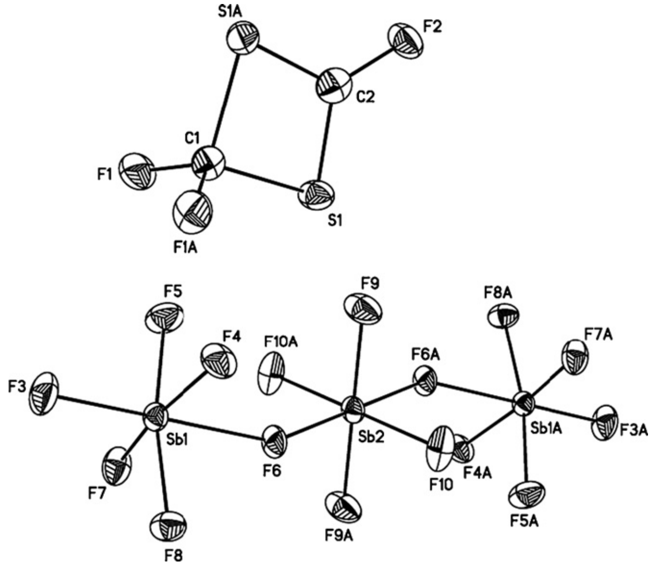
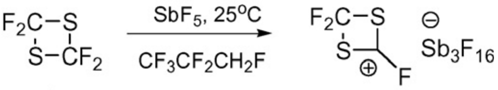


Fig. 1. ORTEP drawing of the salt **6a** with thermal ellipsoids drawn to the 50% probability level.



6 **6a**

Due to low solubility we were not able to characterize this material in solution. The structure of the salt cation **6a** and Sb_3F_{16} counter anion was established by single crystal X-ray diffraction (Fig. 1).

The cation **6a** was prepared earlier by treatment of **6** with Lewis [35] and protic (HF/SbF_5 or $HOSO_2F/SbF_5$) acids [36] and was characterized in solution by NMR spectroscopy. The structure of the hexafluoroarsenate salt of **6a** was reported [37]. It should be pointed out that the bond distances and angles for **6a** obtained in this work compare well with the structure reported earlier [37] (see Table 2) and minor differences in bond distances may be attributed to disorder of hexafluoroarsenate anion in the structure reported earlier [37].

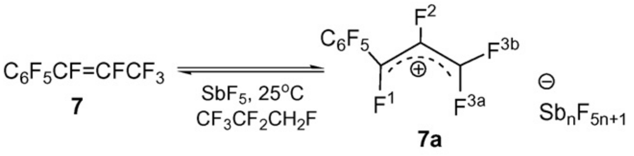
Fluorinated allyl cations in general have lower stability compared to benzylic systems [38,39]. For example, perfluoroallyl cation for a long time was considered to be unstable [2,30] but finally was generated and characterized at low temperature by ^{19}F NMR spectroscopy [29]. The purity of SbF_5 was essential for generation of perfluoroallyl- [29] and methallyl- [40] cations in SO_2ClF or perfluorocyclobutane solvents.

It is well known that the stability of fluorinated allyl cations increases significantly with introduction of electron donating substituents (such as $-OCH_3$ or $-C_6F_5$) to C-1- and C-3- carrying

Table 2
Single crystal X-ray diffraction data for salt **6a** and $C_2F_9S_2As$ [37]

Distances (Å) and angles (°)	**6a**	**$C_2F_9S_2As$** [37]
C2–S1	1.672(5)	1.681(6)
C2–F2	1.294(9)	1.248(12)
C1–S1	1.863(6)	1.848(6)
C1–F1	1.312(6)	1.294(7)
F1–C1–F1a	108.2(7)	110.7(8)
F1–C1–S1	113.6(2)	112.6(2)
C2–S1–C1	77.0(3)	78.4(4)
S1–C1–S1a	95.2(4)	95.0(4)
S1–C2–S1a	110.8(5)	108.3(6)

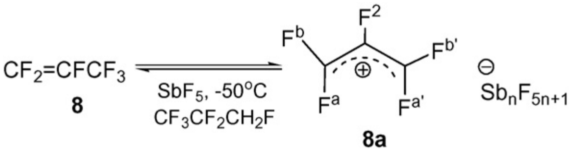
positive charge in an allylic carbocations [7,41–44]. Indeed, the treatment of olefin **7** with excess SbF_5 in HFC-236cb solvent leads to the formation of the known cation **7a** [28], existing in equilibrium with the starting material at 25 °C, according to ^{19}F NMR spectroscopy.



ratio **7 : 7a** - 1 : 1

As it was reported earlier [28], only one isomer of cation **7a** with *trans*- orientation of two fluorine substituents adjacent to C-1 and C-2 of allylic system is present in the solution. It should be also pointed out that in **7a** substituents F^1, F^{3a} and F^{3b} are noticeable less shielded than in *p*-$CH_3OC_6H_4CF{=}CF{-}CF_2^+$ (−0.1, −12.17 and −20.5 ppm for **7a** *vs.* −53.1, −64.8, and −68.6 ppm for *p*-$CH_3OC_6H_4CF{=}CF{-}CF_2^+$ [30]). At this point the reason for such a substantial difference in the chemical shifts of two similar species is not clear, however, it can be attributed to the SO_2 solvent, used for the generation of *p*-$CH_3OC_6H_4CF{=}CF{-}CF_2^+$ (see also [45]).

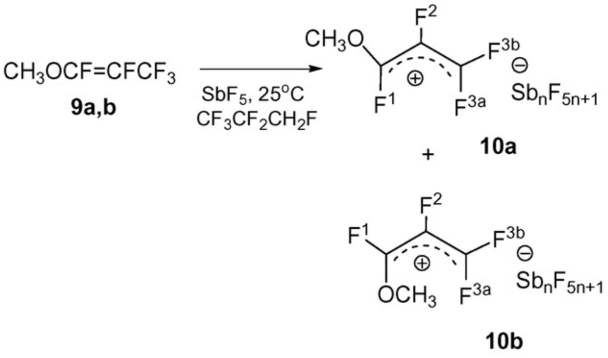
The stability of solutions SbF_5 in HFC-236cb at subzero temperature allows the generation of known perfluoroallyl cation **8a** [29] in this solvent. Indeed, the addition of perfluoropropene (**8**) to the solution of SbF_5 in HFC-236cb resulted in the formation of cation **8a**, observed by ^{19}F NMR in equilibrium with the starting material, even at −50 °C.



ratio **8 : 8a** - 13 : 87

Success in the generation of cation **8a** prompted us to reinvestigate the reaction of SbF_5 and $CH_3OCF{=}CFCF_3$ (**9a** *trans*- and **9b**, *cis*- isomer). The 1-methoxypentafluoroallyl cation is one of the first reported examples of polyfluorinated allylic cations. It was reported 3 years after the discovery of stable salts $[R_2N(RO)C{=}C(CF_3){-}CF_2]^+$ BF_4^- by Rokhlin and co-workers [46] and was generated by the reaction of the **9a**,**b** and SbF_5 in SO_2 solvent [30]. NMR parameters of $CH_3O{-}CF{=}CF{-}CF_2^+$ for a long time remained a mystery, due to the lack of the agreement of reported in [30] values of chemical shifts and coupling constants with data accumulated in last 30 years for a variety of structurally similar fluorinated allyl cations, such as $CH_3OCF{=}C(CF_3){-}CF_2^+$ [41] *p*-$CH_3O{-}C_6H_4CF{=}CF{-}CF_2^+$ [30] or $XCF{=}CF{-}CF_2^+$ (X = H, Cl, Br) [31,38,47,48].

The addition of the olefin **9a**,**b** to the solution of excess SbF_5 in HFC-236cb resulted in complete disappearance of signals of the starting material. Instead, two sets of new signals were observed in ^{19}F NMR spectrum, which were assigned to stable at ambient temperature cations **10a**,**b** (see Table 1, entry 13 and 14; mixture of *trans*- and *cis*- isomers, ratio 60:40). It should be pointed out that, the ratio of **10a**,**b** is independent of the ratio **9a**,**b**, since the same ratio of **10a** to **10b** was obtained from the mixture of *trans*- and *cis*- isomers **9a**,**b** or pure (99%) *trans*- **9a**. Values of chemical shifts and coupling constants of cations **10a** and **10b** are give in Table 1.

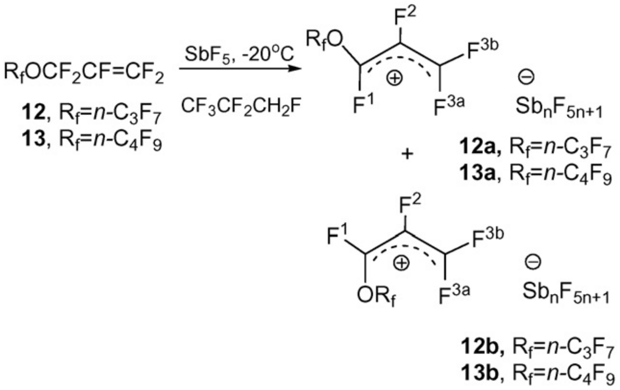


ratio **10a : 10b** - 60 : 40

Further evidence for the existence of cations **10a**,**b**, was obtained in the experiment which employed "traditional" SO_2ClF solvent. The treatment of **9a**,**b** with SbF_5 in this solvent resulted in identical changes in ^1H and ^{19}F NMR spectra and the formation cations **10a**,**b**, with the same ratio of isomers (see Table 1, entry 15 and 16). ^{13}C NMR spectrum acquired in SO_2ClF solvent is also consistent with the structure of allyl cation **10a**,**b** (Table 1, footnote i).

The values of chemical shifts and coupling constants of cations **10a**,**b** generated in HFC-236cb and SO_2ClF solvents are in a good agreement well and also agree well with values for reported for polyfluorinated allyl cations $XCF{=}CFCF_2^+$ (X = H, Cl (**11a**,**b**, see Table 1, entry 17 and 18) and X = Br [7,29,31]). Indeed, the formation of *trans*- and *cis*- isomers was observed for pentafluoroallyl cations $XCF{=}CFCF_2^+$ (X = H, Cl (**11a**,**b**), Br [31]). The conformational stability of isomers is consistent with relatively high rotational barrier around the C–C bond in polyfluorinated allyl cations [38]. The major isomer **10a** has *trans*- orientation of F^1 and F^2 substituents. This conclusion is supported by large values of the coupling constants $^4J_{1-3a}$ = 115 Hz and $^3J_{1-2}$ = 110 Hz, comparable to the corresponding values reported for **11a** ($^4J_{1-3a}$ = 156 Hz and $^3J_{1-2}$ = 118 Hz [31] (Table 1, entry 17). Strong coupling between F_1 and F_{3a} in the *trans*-isomer is the result of through-space interaction of two fluorine substituents located in close proximity [38]. Significantly smaller value of the coupling constant $^4J_{1-3a}$ = 12 Hz in **10b** agrees well with *cis*- orientation of F_1 and F_2 substituents.

Despite the fact that the cation $^+CF_2{=}CFCFOCF_3$ is not stable and was reported to undergo rapid decomposition with elimination of CF_4 at −50 °C [49] homologs containing longer chain perfluoroalkoxy substituents were found to be surprisingly stable. Cations **12a**,**b** and **13a**,**b** were generated by the treatment of perfluoroallyl ethers **12** and **13** with SbF_5 in HFC-236cb solvent at −20 °C and characterized by ^{19}F NMR spectroscopy.



ratio **12a : 12b** - 64 : 36
ratio **13a : 13b** - 63 : 37

It should be pointed out that the ratio of isomers and the values of chemical shifts and coupling constants of the allylic fragment in cations **12a**,**b**, **13a**,**b** are very similar to ratio of isomers and NMR parameters observed for **10a**,**b** (see Table 1, entry 13–16, 19–22). In both cases the large values of $^4J_{1-3a}$ (J = 115–137 Hz) in were observed in *trans*- isomers **12a** and **12b** and the absence of coupling constants $^4J_{1-3a}$ in **12b** and **13b** is in agreement with *cis*-relationship of substituents F^1 and F^2. Self-consistency of NMR data for allylic cations **10a**,**b**; **12a**,**b**; **13a**,**b** also can be viewed as an argument in favor of correct structural assignment of the cations **10a**,**b**.

3. Conclusion

We believe that the striking difference between the outcome of the reaction of **9a**,**b** and SbF_5 can be attributed to the solvent used in the reaction. Sulfur dioxide, used for the generation of $CH_3O–CF{=}CF–CF_2^+$ [30] is relatively basic and may interfere with the step of fluoride anion abstraction by SbF_5 either through the formation of the complex with the Lewis acid or through direct but perhaps, reversible reaction, of SO_2 with the generated carbocation. Such examples are known for highly reactive systems. For example, the mixture of CH_3F/SbF_5 reacts with SO_2, forming the stable salt $CH_3OS{=}O^+\ {}^-Sb_nF_{5n+1}$ [11,12]. While highly electrophilic primary and secondary carbocations were reported to react with SO_2, less reactive tertiary cations can be generated in the same solvent at low temperature [10]. This observation is also consistent with the fact that a several stable fluorinated cations such as polyfluorinated methoxycyclopropenyl [43] and methoxycyclobutenyl [44] cations, $Ar_FCF_2^+$ [24,45] and p-$CH_3O–C_6H_4CF{=}CF–CF_2^+$ [30] were generated and characterized in SO_2. However, accumulated experimental data are indicative that reactive carbocations are able to interact with SO_2 and this solvent should be avoided in reactions involving the formation of highly electrophilic cationic intermediates.

In conclusion, the utility of hydrofluorocarbons as fluorinated solvents for reactions involving highly reactive electrophiles and Lewis acids, was demonstrated in this work. The combination of high oxidative stability, low melting point and sufficient polarity of hydrofluorocarbons, such as $CF_3CF_2CH_2F$ and $(CF_3)_2CFCH_2F$, makes these materials attractive as media for the reactions involving highly electrophilic species.

4. Experimental

Antimony pentafluoride (Galaxy, 99%) was distilled under nitrogen at atmospheric pressure (fraction bp 150–153 °C) and was stored and handled inside a dry box. $C_2F_5CH_2F$ and $(CF_3)_2CFCH_2F$ [23], compounds **9a**,**b** [50] and **12** and **13** [51–55] were prepared using literature procedures and had purity at $\geq$99%. All other starting materials were obtained from commercial sources and used without further purification.

For NMR experiments, 5 mm NMR (Sigma–Aldrich Co.) tubes equipped with a PTFE valve were employed. Such tubes are capable of safely operating with the modest internal pressure generated by liquefied HFC-236cb at ambient temperature. The tube was filled inside of dry box with 0.6–0.9 g of SbF_5 and the corresponding solvent (1–1.5 g) was either condensed into the tube at −78 °C (HFC-236cb) or added as a liquid (HFC-338mmy). The content of NMR tube was agitated at room temperature until all SbF_5 was dissolved and homogeneous solution formed. The tube was cooled down to −78 °C and the substrate (0.1–0.2 g) was either added using pipette (liquids) or was condensed in (gases). Prepared samples were stored in a dry ice before acquiring NMR spectra.

NMR spectra were acquired on either a Varian 400 MHz INOVA three channel spectrometer or a Bruker 400 MHz Avance DRX spectrometer equipped with a 5 mm four nucleus probes. Typical acquisition parameters for ^{19}F spectra were 0.6 s acquisition time, 30 s recycle delay, 8 averaged scans, 90° flip angle (1 μs pulse width) for uniform excitation of the spectral window, and apodization by exponential line broadening using values appropriate for the obtained linewidths. ^1H decoupling, when it was employed, was effected by a Waltz-16 composite pulse sequence. Typical acquisition parameters for ^1H spectra were 1.0 s acquisition time, 30 s recycle delay, 8 averaged scans, and a 30° flip angle. Operation at subambient temperature was achieved by passage of the variable temperature gas through a secondary cooling coil immersed in liquid nitrogen.

X-ray data for salt **6a** ($C_2F_{19}S_2Sb_3$) were collected using a Bruker APEX-II CCD system equipped with a monochromatic molybdenum source at −100 °C. The colorless crystal of dimensions ~0.05 mm × 0.08 mm × 0.08 mm yielded monoclinic cell parameters; a = 12.955(6), b = 7.424(3), c = 17.754(7), β = 108.810(10), space group = $C2/c$. SADABS correction was applied for absorption. The structure was solved and refined using the Shelxtl software package, refinement by full-matrix least squares on F^2, scattering factors from Int. Tab. Vol. C Tables 4.2.6.8 and 6.1.1.4, number of data = 1660, number of restraints = 0, number of parameters = 122, data/parameter ratio = 13.61, goodness-of-fit on F^2 = 1.06, R indices [$I > 4$ sigma(I)] R_1 = 0.030, $wR_2 = 0.051$, R indices(all data) R_1 = 0.045, $wR_2 = 0.056$, max difference peak and hole = 0.94 and −1.05 e/Å^3. The crystal structure has been deposited to the Cambridge Crystallographic Data Center and allocated the deposition number of CCDC 682864.

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References

[1] G.A. Olah, E.B. Baker, J.C. Evans, W.S. Tolgyesi, J.S. McIntyre, I.J. Bastien, J. Am. Chem. Soc. 86 (1964) 1360–1373.
[2] G.A. Olah, Y.K. Mo, Adv. Fluorine Chem. 7 (1973) 69–112.
[3] G.A. Olah, G.K.S. Prakash (Eds.), Carbocation Chemistry, John Wiley & Sons Inc., Hoboken, NJ, 2004.
[4] G.A. Olah, M. Stephenson, J.G. Shih, V.V. Krishnamurthy, G.K.S. Prakash, J. Fluorine Chem. 40 (1988) 319–329.
[5] C.G. Krespan, V.A. Petrov, Chem. Rev. 96 (1996) 3269–3301.
[6] G.A. Olah, G.K. Surya Prakash, J. Sommer, Superacids, John Wiley and Sons, New York, NY, 1985.
[7] V.A. Petrov, V.V. Bardin, Top. Curr. Chem. 192 (1997) 39–95, and references therein.
[8] P.A.W. Dean, R.J. Gillespie, J. Am. Chem. Soc. 91 (1969) 7260–7264.
[9] P.A.W. Dean, R.J. Gillespie, Can. J. Chem. 49 (1971) 1736–1746.
[10] G.A. Olah, D.J. Donovan, H.C. Lin, J. Am. Chem. Soc. 98 (1976) 2661–2663.
[11] P.E. Peterson, R. Brockington, M. Dunham, J. Am. Chem. Soc. 97 (1975) 3517–3518.
[12] P.E. Peterson, R. Brockington, D.W. Vidrine, J. Am. Chem. Soc. 98 (1976) 2660–2661.
[13] G.G. Belen'kii, L.S. German, I.L. Knunyants, G.G. Furin, G.G. Yakobson, Zh. Org. Khim. 12 (1976) 1183–1187.
[14] G.G. Belen'kii, Y.L. Kopaevich, L.S. German, I.L. Knunyants, Dokl. Akad. Nauk SSSR 201 (1971) 603–604 [Chem].
[15] H.S. Booth, C.V. Herrmann, J. Am. Chem. Soc. 58 (1936) 63–66.
[16] J. Bacon, P.A.W. Dean, R.J. Gillespie, Can. J. Chem. 48 (1970) 3413–3424.
[17] J. Bacon, P.A.W. Dean, R.J. Gillespie, Can. J. Chem. 49 (1971) 1276–1283.
[18] G.A. Olah, J. Lukas, J. Am. Chem. Soc. 90 (1968) 933–938.
[19] G.A. Olah, A.M. White, J. Am. Chem. Soc. 89 (1967) 7072–7075.
[20] G.A. Olah, A.M. White, J. Am. Chem. Soc. 91 (1969) 5801–5810.
[21] V.P. Reddy, D.R. Bellew, G.K.S. Prakash, J. Fluorine Chem. 56 (1992) 195–197.
[22] M.V. Galakhov, V.A. Petrov, G.G. Belen'kii, L.S. German, E.I. Fedin, V.F. Snegirev, V.I. Bakhmutov, Izv. Akad. Nauk SSSR, Ser. Khim. (1986) 1063–1072.
[23] G.G. Belen'kii, V.A. Petrov, P.R. Resnick, J. Fluorine Chem. 108 (2001) 15–20.
[24] G.K.S. Prakash, L. Heiliger, G.A. Olah, J. Fluorine Chem. 49 (1990) 33–41.
[25] G.A. Olah, Y.K. Mo, J. Org. Chem. 38 (1973) 2686–2689.
[26] G.A. Olah, M.B. Comisarow, J. Am. Chem. Soc. 91 (1969) 2955–2961.
[27] G.A. Olah, Y.K. Mo, J. Org. Chem. 38 (1973) 2682–2685.

[28] M.V. Galakhov, V.A. Petrov, S.D. Chepik, G.G. Belen'kii, V.I. Bakhmutov, L.S. German, Izv. Akad. Nauk SSSR, Ser. Khim. (1989) 1773–1777.
[29] M.V. Galakhov, V.A. Petrov, V.I. Bakhmutov, G.G. Belen'kii, B.A. Kvasov, L.S. German, E.I. Fedin, Izv. Akad. Nauk SSSR, Ser. Khim. (1985) 306–312.
[30] R.D. Chambers, A. Parkin, R.S. Matthews, J. Chem. Soc. Perkin Trans. 1 (1976) 2107–2112.
[31] S.D. Chepik, M.V. Galakhov, G.G. Belen'kii, V.A. Petrov, L.S. German, V.I. Bakhmutov, Izv. Akad. Nauk SSSR, Ser. Khim. (1988) 2761–2764.
[32] V.D. Shteingarts, in: G.A. Prakash, OlahF G.K.S. (Eds.), Carbocation Chemistry, John Wiley & Sons Inc., Hoboken, NJ, 2004, pp. 159–212.
[33] Y.V. Pozdnyakovich, V.D. Shteingarts, J. Fluorine Chem. 4 (1974) 296–316.
[34] Y.V. Pozdnyakovich, V.D. Shteingarts, J. Fluorine Chem. 4 (1974) 317–326.
[35] A. Waterfeld, R. Mews, Chem. Ber. 118 (1985) 4997–5005.
[36] A. Haas, W. Wanzke, Chem. Ber. 120 (1987) 429–433.
[37] J. Antel, K. Harms, P.G. Jones, R. Mews, G.M. Sheldrick, A. Waterfeld, Chem. Ber. 118 (1985) 5006–5008.
[38] V.I. Bakhmutov, M.V. Galakhov, Usp. Khim. 57 (1988) 1467–1487.
[39] G.G. Belen'kii, J. Fluorine Chem. 77 (1996) 107–116.
[40] V.A. Petrov, G.G. Belen'kii, M.V. Galakhov, V.I. Bakhmutov, L.S. German, E.I. Fedin, Izv. Akad. Nauk SSSR, Ser. Khim. (1984) 2811–2813.
[41] V.F. Snegirev, M.V. Galakhov, V.A. Petrov, K.N. Makarov, V.I. Bakhmutov, Izv. Akad. Nauk SSSR, Ser. Khim. (1986) 1318–1325.
[42] V.F. Snegirev, M.V. Galakhov, K.N. Makarov, V.I. Bakhmutov, Izv. Akad. Nauk SSSR, Ser. Khim. (1985) 2302–2309.
[43] B.E. Smart, J. Org. Chem. 41 (1976) 2377–2379.
[44] B.E. Smart, G.S. Reddy, J. Am. Chem. Soc. 98 (1976) 5593–5597.
[45] The reviewer suggested that in this case the chemical shift computations could help to rule out actual electronic effects and strengthen the solvent effect argument.
[46] I.L. Knunyants, Y.G. Abduganiev, E.M. Rokhlin, P.O. Okulevich, N.I. Karpushina, Tetrahedron 29 (1973) 595–601.
[47] V.I. Bakhmutov, M.V. Galakhov, B.A. Kvasov, E.I. Fedin, Izv. Akad. Nauk SSSR, Ser. Khim. (1988) 2277–2281.
[48] M.V. Galakhov, V.A. Petrov, G.G. Belen'kii, V.I. Bakhmutov, L.S. German, E.I. Fedin, Izv. Akad. Nauk SSSR, Ser. Khim. (1986) 1057–1063.
[49] S.D. Chepik, G.G. Belen'kii, L.S. German, Izv. Akad. Nauk SSSR, Ser. Khim. (1991) 1926–1928.
[50] M.D. Bargamova, Y.A. Cheburkov, B.L. Dyatkin, P.V. Petrovskii, I.L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim. (1967) 611–614.
[51] C.G. Krespan (to DuPont), US Pat. 4,273,728 (1981).
[52] C.G. Krespan (to DuPont), US Pat. 4,304,927 (1981).
[53] C.G. Krespan (to DuPont), US Pat. 4,275,225 (1981).
[54] C.G. Krespan (to DuPont), US Pat. 4,292,449 (1981).
[55] C.G. Krespan (to DuPont), WO 9,109,010 (1991).