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A widely varying range of products in reactions of $C_6F_5BrF_2$, $C_6F_5IF_2$, and $C_6F_5IF_4$ with Lewis acids of different strength

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ABSTRACT

The relative fluoride donor ability: $C_6F_5BrF_2 > C_6F_5IF_2 > C_6F_5IF_4$ was outlined from reactions with Lewis acids of graduated strength in different solvents. Fluoride abstraction from $C_6F_5HalF_2$ with $BF_3{\cdot}NCCH_3$ in acetonitrile (donor solvent) led to $[C_6F_5HalF{\cdot}(NCCH_3)_n][BF_4]$. The attempted generation of $[C_6F_5BrF]^+$ from $C_6F_5BrF_2$ and anhydrous HF or BF_3 in weakly coordinating SO_2ClF gave C_6F_5Br besides bromoperfluorocycloalkenes C_6BrF_7 and 1-BrC_6F_9. In reactions of $C_6F_5IF_2$ with SbF_5 in SO_2ClF the primary observed intermediate (^{19}F NMR, below 0 °C) was the 4-iodo-1,1,2,3,5,6-hexafluorobenzenium cation, which converted into C_6F_5I and 1-IC_6F_9 at 20 °C. The reaction of $C_6F_5IF_4$ with SbF_5 in SO_2ClF below −20 °C gave the cation $[C_6F_5IF_3]^+$ which decomposed at 20 °C to C_6F_5I, 1-iodoperfluorocyclohexene, and iodoperfluorocyclohexane. Principally, the related perfluoroalkyl compound $C_6F_{13}IF_4$ showed a different type of products in the fast reaction with AsF_5 in CCl_3F (−60 °C) which resulted in C_6F_{14}. Intermediate and final products of $C_6F_5HalF_{n-1}$ (n = 3, 5) with Lewis acids were characterized by NMR in solution. Stable solid products were isolated and analytically characterized.

1. Introduction

Bis(organyl)iodonium salts [RR′I][Y] are well known compounds which are widely used in organic synthesis [1–7]. Bis(organyl)bromonium salts [RR′Br][Y] are less investigated although some progress was achieved in the last two decades [2–4,8–11]. Only little is known about the related organyl(fluoro)halonium salts. Bubbling of BF_3 into solutions of perfluoroalkyliodine difluoride in CH_2Cl_2 at −60 °C led to a precipitate which gave in subsequent reactions with electron-rich aromatic compounds (C_6H_6, $C_6H_5CH_3$) perfluoroalkyl(aryl)iodonium tetrafluoroborates. The nature of the primary precipitate was not elucidated [12,13]. Organyliodine tetrafluorides R_FIF_4 (R_F represents perfluorinated alkyl, alkenyl, cycloalkenyl, and aryl groups) did not react with BF_3 in 1,1,1,3,3-pentafluorobutane (PFB) at −20 to 22 °C [14]. When the Lewis acid was perfluoroorganyldifluoroborane, $R'BF_2$, the iodonium salt $[R_F(R'_F)IF_{n-3}][BF_4]$ (n = 5) was formed rather than the salt $[R_FIF_{n-2}][R'_FBF_3]$ (see review [4]). Attempted reactions of CF_3IF_4 with AsF_5 [15] or of CF_3IOF_2 with BF_3, AsF_5, or SbF_5 [16] resulted in the decomposition of the iodine(V) compounds and formation of CF_4. Fluoride abstraction from $C_6F_5IF_2$ and $C_6F_5IF_4$ under the action of SbF_5 in SO_2ClF at low temperatures was reported to give solutions of $[C_6F_5IF]Y$ [17] and $[C_6F_5IF_3]Y$ [18], respectively. Seppelt prepared the salt $[C_6H_5IF_3][SbF_6]$ from $C_6H_5IF_4$ and SbF_5 in anhydrous HF (aHF) at −30 °C and characterized it by X-ray structural analysis, ^1H, ^{19}F NMR, and Raman spectra [19]. In all cases, the salts $[ArIF_{n-2}][Sb_mF_{5m+1}]$ (n = 3, 5) were intrinsically unstable and decomposed above −20 to 0 °C to unknown products. To our knowledge, the preparation or detection of any organyl(fluoro)bromonium salts was not reported so far.

Continuing our systematic research in the field of fluoroorganohalogen fluorides, we investigated the interaction of $C_6F_5BrF_2$ (**1**), $C_6F_5IF_2$ (**2**), and $C_6F_5IF_4$ (**3**) with Lewis acids of different strength in donating (acetonitrile), weakly coordinating (SO_2ClF, CH_2Cl_2, or 1,1,1,3,3-pentafluoropropane (PFP)) and acidic (anhydrous HF) solvents.

2. Results

2.1. *Reactions of $C_6F_5HalF_2$ (Hal = Br, I) with $BF_3{\cdot}NCCH_3$ in the presence of the strongly coordinating solvent acetonitrile*

The addition of $BF_3{\cdot}NCCH_3$ in CD_3CN to a cold (−78 °C) solution of $C_6F_5BrF_2$ (**1**) in CD_2Cl_2 led to the complete consumption of **1** and formation of the new species (**1a**) (Eq. (1)) which displayed ^{19}F resonances at −86.5 (s, $\tau_{1/2}$ = 30 Hz, 1F, BrF), −128.5 (m, 2F, $F^{2,6}$), −135.4 (ttd, $^3J(F^4,F^{3,5})$ = 22 Hz, $^4J(F^4,F^{2,6})$ = 9 Hz, $^6J(F^4,BrF)$ = 9 Hz, 1F, F^4), −154.7 (m, 2F, $F^{3,5}$), and −151.4 ($[BF_4]^-$) ppm (−78 °C). In a similar way, the reaction of $C_6F_5IF_2$ (**2**) with $BF_3{\cdot}NCCH_3$ in

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Table 1
^{19}F NMR spectral data of $C_6F_5HalF_2$ and $[(C_6F_5)_2Hal][BF_4]$ (CD_3CN, 24 °C)[a].

Compound	δ (F), ppm				Ref.
	$F^{2,6}$	F^4	$F^{3,5}$	Hal–F[b]	
$C_6F_5BrF_2$[c]	−133.2	−144.0	−156.8	−44.5	[20]
$C_6F_5BrF_2$	−134.0	−143.6	−156.7	−49.0	[20]
$[(C_6F_5)_2Br][BF_4]$	−129.3	−139.6	−155.2		[10]
$C_6F_5IF_2$[d]	−122.1	−143.6	−156.9	−158.6	[21]
$C_6F_5IF_2$	−122.9	−144.5	−157.0	−160.5	[21]
$[(C_6F_5)_2I][BF_4]$	−120.4	−141.4	−155.7		[22]

[a] The signal of counteranion $[BF_4]^-$is not given.

[b] Unresolved signal.

[c] In CCl_3F.

[d] In CD_2Cl_2.

acetonitrile at −40 °C resulted in the new species (**2a**) (Eq. (2)), which was characterized by not resolved ^{19}F resonances at −119.9 (2F, $F^{2,6}$), −140.7 (1F, F^4), −155.9 (m, 2F, $F^{3,5}$), −191.2 (1F, I*F*), and −147.6 (broad, $[BF_4]^-$) ppm (−40 °C). Both cations **1a** and **2a** showed deshielding of the carbon-bonded fluorine atoms with respect to the corresponding precursors $C_6F_5HalF_2$ (Table 1). This trend of shifts is in agreement with a stronger polarizing Hal atom in the cations (cf. similar trends for $[(C_6F_5)_2Hal]^+$ cations, Table 1). However, the still remaining fluorine atom at bromine or iodine is strongly shielded by 30–35 ppm with respect to the fluorine atoms in the parent molecules $C_6F_5HalF_2$. Noteworthy, the unresolved C_6F_5 resonances and the broad deshielded $[BF_4]^-$ resonance of **2a** are clear hints that in case of the iodo compound the cation and the anion are not solvent separated independent species.

$$\underset{\mathbf{1}}{C_6F_5BrF_2} + BF_3\cdot NCCH_3 \xrightarrow[-78^\circ C]{CD_2Cl_2+CD_3CN(5:1)} \underset{\mathbf{1a}}{[C_6F_5BrF\cdot(NCCH_3)n][BF_4]} \quad (1)$$

$$\underset{\mathbf{2}}{C_6F_5IF_2} + BF_3\cdot NCCH_3 \xrightarrow[-40^\circ C]{MeCN} \underset{\mathbf{2a}}{[C_6F_5IF\cdot(NCCH_3)_n][BF_4]} \quad (2)$$

Warming of **1a** in CD_2Cl_2/CD_3CN (5:1) from −78 to 22 °C was accompanied by a brown coloration and caused the formation of bromopentafluorobenzene (**4**) and traces of 1-bromoheptafluorocyclohexa-1,4-diene (**5**). The solution of **2a** in MeCN was thermally more stable. Thus, a sweep of temperature from −40 to 24 °C and back showed no changes of the ^{13}C and ^{19}F NMR signals of the C_6F_5 moiety, only the I–F and the $[BF_4]^-$ signals underwent reversible broadening. Maintaining the MeCN solution of **2a** over hours at room temperature was accompanied by a change from colorless to brown and a slow decomposition. The ^{19}F NMR spectra displayed the slow formation of iodopentafluorobenzene (**8**). Thus, the molar ratio **2a**:**8** was 66:34 after 17 h and 0:100 after 48 h (Eq. (3)).

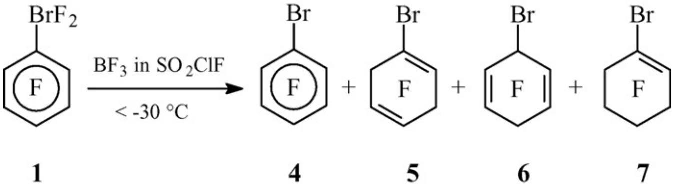
$$\begin{array}{l}[C_6F_5\,Hal\,F\cdot(NCCH_3)_n][BF_4] \\ Hal = Br\,(\mathbf{1a},\mathbf{4}),\,I(\mathbf{2a},\mathbf{8})\end{array} \xrightarrow[20-22^\circ C]{CH_3CN} C_6F_5\,Hal + [BF_4]^- + \cdots \quad (3)$$

Despite of the strong coordination property of MeCN (DN = 14.1), compound **2a** maintained its electrophilic character and formed pentafluorophenyl(mesityl)iodonium tetrafluoroborate (**14**) in the reaction with mesitylene (MeCN, −40 °C) (Eq. (4)).

$$\begin{array}{l}\underset{\mathbf{2a}}{[C_6F_5IF\cdot(NCCH_3)_n][BF_4]} + 1,3,5\text{-}C_6H_3(CH_3)_3 \xrightarrow{MeCN} \\ \quad \underset{\mathbf{14}}{[(2,4,6-C_6H_2(CH_3)_3)(C_6F_5)I][BF_4]} + H^+_{solv} + [BF_4]^-\end{array} \quad (4)$$

2.2. *Reactions of $C_6F_5HalF_2$ (Hal = Br, I) with BF_3 in weakly coordinating solvents*

Bubbling of BF_3 into the cold (−30 °C) suspension of $C_6F_5BrF_2$ in SO_2ClF caused the fast conversion into C_6F_5Br, 1-bromoheptafluorocyclohexa-1,4-diene (**5**), 3-bromoheptafluorocyclohexa-1,4-diene (**6**), and 1-bromononafluorocyclohexene (**7**) (molar ratio 38:21:13:28) (^{19}F NMR) (Eq. (5)). No ^{19}F resonances for the cation $[C_6F_5BrF]^+$ or related species were present.



(5)

Reactions of $C_6F_5IF_2$ with BF_3 in weakly coordinating solvents were performed in modified ways. Bubbling of BF_3 (excess) into a solution of **2** in PFP at −20 °C or stirring a CH_2Cl_2 solution of **2** at −40 °C under the pressure of BF_3 (excess) resulted in a yellow precipitate (**2b**). The solution of the latter in cold (−40 °C) MeCN showed ^{19}F signals of $C_6F_5IF_2$, $[C_6F_5IF{\cdot}(NCCH_3)_n][BF_4]$ (**2a**), and $[(C_6F_5)_2I][BF_4]$ (admixture). The nature of **2a** was proved by conversion into the iodonium salt **14** using mesitylene. Dissolution of **2b** in HF which contained a small amount of water led to $C_6F_5IF_2$ and $[BF_4]^-$ (2:1) (^{19}F NMR). Based on these results, we conclude that the precipitate **2b** is the salt $[(C_6F_5IF)_2F][BF_4]$ with the dinuclear, fluoride-bridged iodonium constitution (Eqs. (6)–(8)). Our conclusion has an analogy in the $[Xe_2F_3]^+$ cation formed from $[XeF]^+$ and XeF_2.

$$\underset{\mathbf{2}}{C_6F_5IF_2} + BF_3 \xrightarrow[-40^\circ C,\,slow]{PFP\,or\,CH_2Cl_2} \langle[C_6F_5IF][BF_4]\rangle \xrightarrow[fast]{+C_6F_5IF_2} \underset{\mathbf{2b}}{[(C_6F_5IF)_2F][BF_4]} \quad (6)$$

$$\begin{array}{l}[(C_6F_5IF)_2F][BF_4] \\ \quad + n\,CH_3CN \xrightarrow[-40^\circ C]{} \underset{\mathbf{2a}}{[C_6F_5IF\cdot(NCCH_3)_n][BF_4]} + C_6F_5IF_2\end{array} \quad (7)$$

$$[(C_6F_5IF)_2F][BF_4] + H_2O \xrightarrow{HF} 2\,C_6F_5IF_2 + [H_3O][BF_4] \quad (8)$$

2.3. *Reactions of $C_6F_5HalF_2$ (Hal = Br, I) with anhydrous HF*

Anhydrous HF combines the properties of a strong protic acid (super acidity), a Lewis acid of medium strength, and a polar solvent. In general, dissolution of salts MX in aHF resulted in "weakly solvated" cations $[M(FH)_m]^+$ and strongly solvated anions $[X(HF)_n]^-$. Strongly polar molecules can dissociate in aHF. Dissolution of BrF_3 in aHF results in the ionisation via fluoride abstraction [23,24] (Eq. (9)). This information suggested to examine the reaction of $C_6F_5BrF_2$ with aHF. Surprisingly, dissolution of **1** in aHF at −40 or −80 °C resulted in the fast conversion into products **4**, **5**, **6**, and **7** (molar ratio 17:73:4:6) which were also obtained in the reaction of **1** with BF_3 (Lewis acid of medium strength) in SO_2ClF (Eq. (10)).

$$BrF_3 + n\,HF \overset{aHF}{\rightleftharpoons} [BrF_2][F(HF)_n] \quad (9)$$

$$C_6F_5BrF_2 \xrightarrow[-80\,or\,-40^\circ C]{aHF} \mathbf{4} + \mathbf{5} + \mathbf{6} + \mathbf{7} + \cdots \quad (10)$$

In contrast, solutions of $C_6F_5IF_2$ in aHF showed no decomposition at 20–22 °C within days, The extreme broadening of the IF_2

signal (^{19}F NMR) indicated a fast exchange of the hypervalently bonded fluorine atoms with that of the solvent [20].

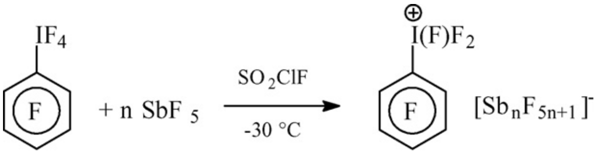
2.4. Reaction of $C_6F_5IF_2$ with SbF_5 in SO_2ClF

To achieve the complete ionisation of $C_6F_5IF_2$ to $[C_6F_5IF]^+$, we employed the strong fluoride acceptor antimony pentafluoride. The reaction of **2** with SbF_5 (excess) in SO_2ClF at −20 °C resulted in a deep green solution. Its ^{19}F NMR spectrum contained three resonances of equal intensity at −95.8, −111.8, and −135.8 ppm besides broad resonances of fluorine bonded to Sb^V at −90 and −110 ppm. The analysis of the ^{19}F–^{19}F couplings allowed to assign the triple of resonances to the 4-iodo-1,1,2,3,5,6-hexafluorobenzenium cation (**2c**). This re-investigation allowed to reject the previously proposed pentafluorophenyl(fluoro)iodonium constitution $[C_6F_5IF]^+$ (**2d**) [17]. Characteristic data of this spectrum and for comparison the spectral data of the related 4-R-1,1,2,3,5,6-hexafluorobenzenium cations (R = F, Cl, OH) are presented in Table 2.

The spectrum of **2c** did not change in the temperature range from −50 to −10 °C, but at 20 °C the resonances of **2c** disappeared within 1–2 h and parallel signals of 1-iodononafluorocyclohexene (**9**) and of the $[(C_6F_5)_2I]^+$ cation appeared as major products. The fact that after the complete decomposition of **2c** the solution was still deep green, shows that this color did not derive from **2c**. The color is presumably attributed to the radical cation $[C_6F_5I]^{\bullet +}$ which possesses a very high extinction coefficient and is formed under the same conditions from traces of C_6F_5I and SbF_5 [27,28]. After decomposition of **2c** and dilution of the deep green solution with aHF and subsequent hydrolysis (0 °C), C_6F_5I (**8**), 1-iodononafluorocyclohexene (**9**), 1-iodo-3-oxopentafluorocyclohexa-1,4-diene (**11**), 1-iodo-6-oxopentafluorocyclohexa-1,4-diene (**12**), and $[(C_6F_5)_2I][F(HF)_n]$ were isolated in ca. 72% overall yield (molar ratio 42:42:3:3:10) (^{19}F NMR) (Scheme 1).

2.5. Reaction of $C_6F_5IF_4$ with fluoride acceptors

Pentafluorophenyliodine tetrafluoride (**3**) is poorly soluble in aHF. Its ^{19}F NMR in aHF (0 °C) consists of resonances at −12.1 (s, $\tau_{1/2}$ = 78 Hz, IF_4), −127.9 (s, $\tau_{1/2}$ = 46 Hz, 2F, $F^{2,6}$), −135.4 (tt, $^3J(F^4,F^{3,5})$ = 19 Hz, $^4J(F^4,F^{2,6})$ = 10 Hz, 1F, F^4), −157.3 (m, 2F, $F^{3,5}$) and did not change within days at 20 °C. $C_6F_5IF_4$ resists to acidified aHF (aHF/NbF_5) and to BF_3 in 1,1,1,3,3-pentafluorobutane as well [14]. In contrast, the reaction between $C_6F_5IF_4$ and SbF_5 (excess) in SO_2ClF occurred fast at −35 °C and resulted in a yellow solution of pentafluorophenyl(trifluoro)iodonium fluoroantimonate (**3d**) (Eq. (11)). The ^{19}F NMR spectrum of the latter (−30 °C) consisted of two resonances of fluorine atoms bonded to iodine at δ 2.0 (td, $^4J(F_2I,F^{2,6})$ = 16 Hz, $^2J(F_2I,IF)$ = 51 Hz, 2F, $IF_2(F)$) and at −43.2 (t, $^2J(FI,IF_2)$ = 51 Hz, 1F, $IF_2(F)$) ppm, respectively, and of the three signals of the pentafluorophenyl group at δ −125.7 (m, 2F, $F^{2,6}$), −126.6 (tt, $^3J(F^4,F^{3,5})$ = 18 Hz, $^4J(F^4,F^{2,6})$ = 14 Hz, 1F, F^4), and −151.0 (m, 2F, $F^{3,5}$) ppm. The broad signals of the counteranion $[Sb_nF_{5n+1}]^-$ were located at −88 and −110 ppm (cf. [18]). For comparison, the related compounds $C_6F_5IF_4$, IF_5, and $[IF_4][SbF_6]$ were characterized by their ^{19}F chemical shifts δ −9.0 (IF_4), −130.1 ($F^{2,6}$), −143.3 (F^4), and −158.3 ($F^{3,5}$) ppm ($C_6F_5IF_4$ in CD_2Cl_2), 57.5 ($1F_{ax}$) and 10.1 ($4F_{eq}$) ppm (IF_5 in CH_2Cl_2) [29], 21.8 (s, $[IF_4]^+$), and −109 ppm (br s, $[SbF_6]^-$) ($[IF_4][SbF_6]$ in SO_2ClF (−10 °C). The solution of the closely related salt $[C_6H_5IF_3][SbF_6]$ in SO_2 (−60 °C) showed a single ^{19}F resonance at −39.9 ppm (s, IF_4) and a broad Sb^V–F resonance at −111.4 ppm while the precursor $C_6H_5IF_4$ displayed the IF_4 signal at −25.6 ppm (in ether) [19].



(11)

3 **3d**

Neither the chemical shifts nor the magnitudes of the J(F,F) couplings were changed when the solution of **3d** was kept at −20 °C (30 min) and at 0 °C (30 min). At 20 °C the initially yellow solution of **3d** became deep green (the origin of the deep green color was discussed above) within 20–30 min. The change of color was accompanied by 20–25% of decomposition. The observed main products were iodononafluorocyclohexene (**9**) and an equal amount of the 4-iodohexafluorobenzenium cation (**2c**) (^{19}F NMR). After 2 h salt **3d** was consumed completely. Dilution of the still deep green solution with aHF, subsequent hydrolysis (0 °C), and extraction of the products with CH_2Cl_2 gave **8**, **9**, iodoundecafluorocyclohexane (**10**), and $[(C_6F_5)_2I][F(HF)_n]$ (molar ratio 53:26:17:4) (overall yield ca. 78%) besides traces of unknown compounds (^{19}F NMR) (Scheme 2).

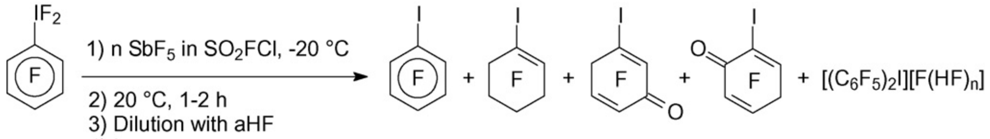
3. Discussion

The results display a decreasing fluoride donor ability in the series $C_6F_5BrF_2 > C_6F_5IF_2 > C_6F_5IF_4$. The fate of the pentafluorophenyl(fluoro)halonium cation $[C_6F_5HalF]^+$ (or a structurally

Table 2
^{19}F NMR spectral data of 4-R-1,1,2,3,5,6-hexafluorobenzenium fluoroantimonates (SO_2ClF, −40 °C).

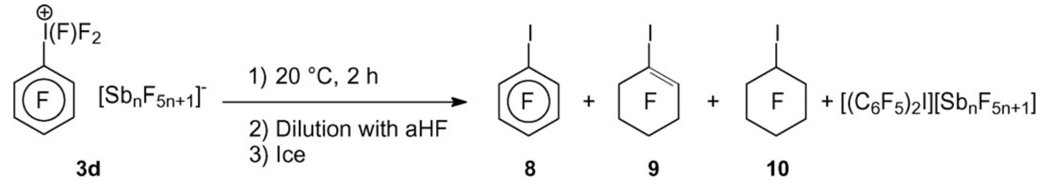
R	δ (F), ppm			Coupling constants
	$F^{1,1}$	$F^{2,6}$	$F^{3,5}$	
F [25][a]	−131	−55	−142	$^3J(F^1,F^2)$ = 23 Hz, $^4J(F^1,F^3)$ = 6 Hz
Cl [25]	−132	−71	−126	$^3J(F^1,F^2)$ = 22 Hz, $^4J(F^1,F^3)$ = 8 Hz, $^3J(F^2,F^3)$ = 5 Hz, $^4J(F^3,F^5)$ = 5 Hz
I[b]	−135.8	−95.8	−111.8	$^3J(F^1,F^2)$ = 25 Hz, $^4J(F^1,F^3)$ = 8 Hz, $^3J(F^2,F^3)$ = 4 Hz, $^4J(F^3,F^5)$ = 4 Hz
OH [26][c]	−124.5	−99.4	−148.3	$^3J(F^1,F^2)$ = 23 Hz, $^4J(F^1,F^3)$ = 7.5 Hz

[a] δ = 34 (d $^3J(F^4,F^3)$ = 28 Hz, d $^3J(F^4,F^5)$ = 28 Hz, d $^4J(F^4,F^2)$ = 109 Hz, d $^4J(F^4,F^6)$ = 109 Hz, 1F, F^4) ppm.
[b] This work.
[c] In SO_2 at −50 °C.

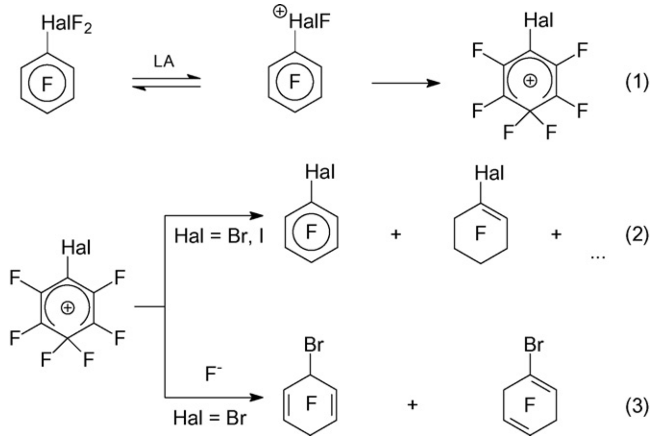


2 **8** **9** **11** **12**

Scheme 1.

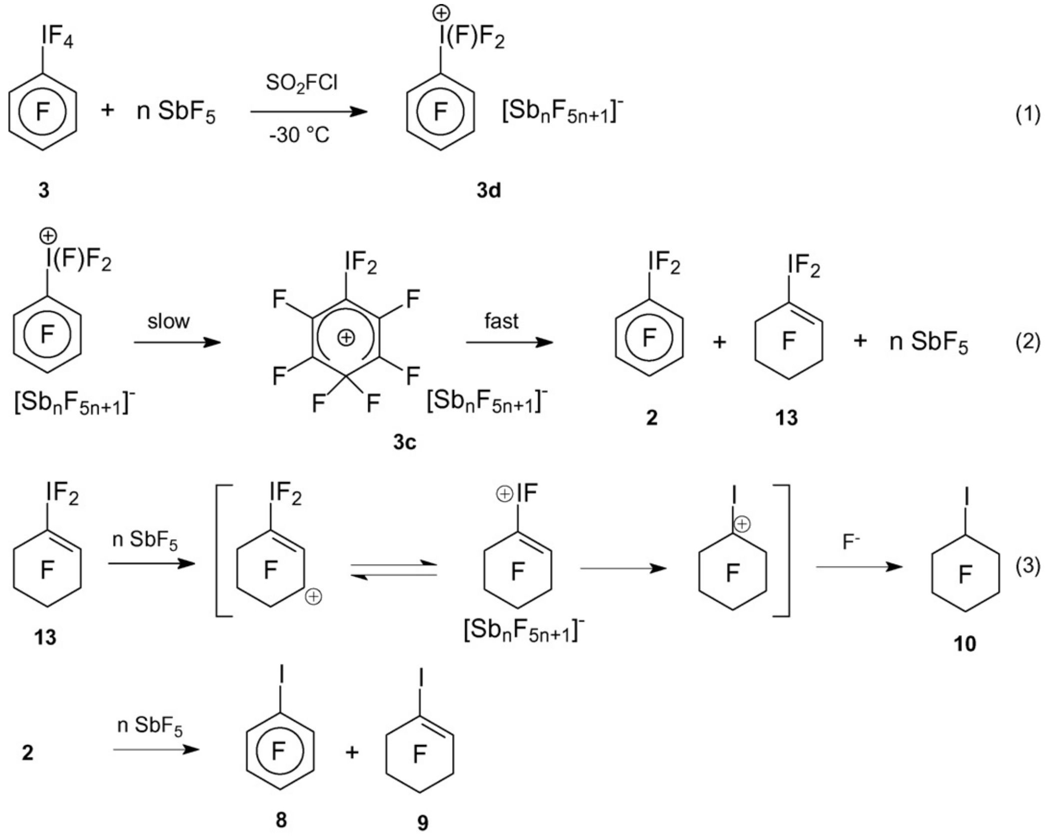


Scheme 2.



Scheme 3.

related species) is determined by the coordinating property of the solvent. When fluoride abstraction from $C_6F_5HalF_2$ occurred in acetonitrile, the cation $[C_6F_5HalF]^+$ is stabilized by base coordination $[C_6F_5HalF{\cdot}(NCCH_3)_n][BF_4]$ (Hal = Br, I), and the latter can be characterized by multi-NMR spectroscopy. When the fluoride abstraction from $C_6F_5HalF_2$ by Lewis acids occurred in acidic (aHF) or weakly coordinating solvents, the intermediate $[C_6F_5HalF]^+$ is insufficiently stabilized by coordination and quickly rearranged to the (halo)hexafluorobenzenium cation which finally disproportionated and formed C_6F_5Hal and haloperfluorocycloalkenes. The driving force of rearrangement from the halonium cation to the benzenium cation (Scheme 3, route (1)) is the formation of the stronger C–F bond compared with the weaker Hal–F bond. Furthermore, the delocalization of the positive charge over five carbon atoms in the (halo)hexafluorobenzenium cation is favored over the charge localization in $[C_6F_5HalF]^+$. The formation of the final main reaction products, halopentafluorobenzene and haloperfluorocycloalkenes can be explained by further transformations of the polyfluorinated arenium cations [30]. When Hal = Br and LA = BF_3, the corresponding benzenium cation is a short-living species with high fluoride affinity and disproportionates to C_6F_5Br and 1-BrC_6F_9 (Scheme 3, route (2)) and parallel it adds fluoride and converts into bromoheptafluorocyclohexadienes **5** and **6** (Scheme 3, route (3)). When Hal = I and LA = SbF_5, the iodohexafluorobenzenium cation was the primary observed reaction intermediate which slowly formed C_6F_5I and 1-IC_6F_9 at 20 °C (Scheme 3, route (2)). The relative contribution of route (3), the addition of fluoride



Scheme 4.

to the benzenium cation **2c**, was negligible because of the low fluoride donor ability of the fluoroantimonate counteranion and the excess of SbF_5 present in the solution.

The pentafluorophenyl(trifluoro)iodonium cation $[C_6F_5IF_3]^+$ (**3d**) is a more stable species than $[C_6F_5IF]^+$ and decomposed above 0 °C. We assume that the conversion of **3d** (Scheme 4, route (1)) proceeds via the polyfluorinated benzenium cation **3c** (Scheme 4, route (2)). In contrast to **2c**, the latter is a highly unfavored species because the strong electron-withdrawing group IF_2 is bonded to the positively charged atom C-4, and thereupon it quickly formed $C_6F_5IF_2$ and 1-$IF_2C_6F_9$ (**13**). Further conversions of the intermediately formed $C_6F_5IF_2$ in the presence of SbF_5, which were discussed above, give **2c**, **8**, and **9**. The possible route from **13** to iodoundecafluorocyclohexane (**10**) is presented in Scheme 4 (route 3).

In all cases the reaction products which derived from $C_6F_5HalF_{n-1}$ ($n = 3, 5$) were halogen-containing perfluoroorganics. C_6F_6, C_6F_8, C_6F_{10}, and/or C_6F_{12} as products of C–Hal cleavage were *not* formed. This contrasted with reported qualitative observations of carbon–iodine bond cleavage in reactions of the perfluoroalkyl compounds CF_3IF_4 and CF_3IOF_2 with fluoride acceptors (BF_3, AsF_5, or SbF_5) [14,15]. To verify this important distinction to $C_6F_5HalF_{n-1}$ ($n = 5$) compounds we have treated $C_6F_{13}IF_4$ with AsF_5 in CCl_3F and obtained perfluorohexane in >90% yield (Eq. (12)). Organoiodine-containing products were not found.

$$C_6F_{13}IF_4 \xrightarrow{AsF_5 \text{ in } CCl_3F} C_6F_{14} \qquad (12)$$

Likely, that an irreversible fluorodeiodination of the intermediate cation $[C_6F_{13}IF_3]^+$ occurred caused by the high partial positive charge at C-1, which bears two fluorine atoms and a perfluoroalkyl tail. The absence of a positive partial charge at C-1 in case of the cation $[C_6F_5IF_3]^+$ prevents a fluorodeiodination and favors alternative reaction channels (Scheme 4).

Finally, we need to comment the formation of the by-product $[(C_6F_5)_2I][SbF_6]$, in reactions of $C_6F_5IF_n$ ($n = 3, 5$) with SbF_5 in SO_2ClF. Probably, this salt is formed via an one electron oxidation of C_6F_5I by SbF_5 to the radical cation $[C_6F_5I]^{\bullet+}$ [27] which undergoes attacks on C_6F_5I (Eq. (13)).

$$C_6F_5I \overset{SbF_5}{\rightleftharpoons} \underset{\text{deep green}}{[C_6F_5I]^{\bullet+}} \xrightarrow{C_6F_5I} [(C_6F_5)_2I]^+ + I^\bullet (\rightarrow I_2) \qquad (13)$$

Evidently, a freshly prepared deep blue solution of C_6F_5I and SbF_5 (threefold excess) in SO_2ClF (−30 °C) did neither display ^{19}F resonances of iodopentafluorobenzene nor of other fluoroorganic products, but warming to 20 °C caused a deep green coloration and after 1.5 h at 20 °C, signals of the cation $[(C_6F_5)_2I]^+$ were detected. After 14 h at 20 °C and dilution with aHF the hydrolysis of the deep green solution gave C_6F_5I and $[(C_6F_5)_2I][F(HF)_n]$ (74:26, molar). In an other experiment, the deep green solution of C_6F_5I in SbF_5/SO_2ClF was kept at 20 °C over a period of 5 days. After hydrolysis, extraction and subsequent anion metathesis with $Na[BF_4]$, the salt $[(C_6F_5)_2I][BF_4]$ was isolated in 75% yield. Noteworthy, that neither the spectra of solutions of decomposing $C_6F_5IF_2$ nor of $C_6F_5IF_4$ in SbF_5/SO_2ClF at 20 °C did display the signals of C_6F_5I, although after the final step of hydrolysis the latter was the major product. This phenomenon is explained by a fast electron exchange between C_6F_5I and the paramagnetic radical cation $[C_6F_5I]^{\bullet+}$ [27].

4. Experimental

The NMR spectra were recorded on Bruker AVANCE 300 (75.47 MHz, ^{13}C; 282.40 MHz, ^{19}F) and Bruker DRX 500 (125.75 MHz, ^{13}C; 470.59 MHz, ^{19}F) spectrometers. The chemical shifts are referenced to TMS (^{13}C), and CCl_3F (^{19}F, with C_6F_6 as secondary reference (−162.9 ppm)), respectively. The composition of the reaction mixtures and the yields of products were determined by ^{19}F NMR spectroscopy using the internal quantitative standards C_6F_6 or $C_6H_5CF_3$. Polyfluorocycloalkenes **5**, **6**, **7**, and **9** were identified by ^{19}F NMR spectroscopy [31].

Iodopentafluorobenzene (Bristol Organics), 1,1,1,3,3-pentafluoropropane (PFP) (Honeywell), and boron trifluoride (Messer Griesheim) were used as supplied. Antimony pentafluoride was twice distilled under an atmosphere of dry argon. Acetonitrile (Fluka) and dichloromethane (Fluka) were purified and dried as described in Ref. [32]. SO_2ClF was purified by shaking with mercury and subsequently distilled over SbF_5. Anhydrous HF was stored over CoF_3. $C_6F_5BrF_2$ [20], $C_6F_5IF_2$ [21], $C_6F_5IF_4$ [29], $C_6F_{13}IF_4$ [14], and $BF_3{\cdot}NCCH_3$ [33] were prepared as described.

All manipulations were performed in FEP (block copolymer of tetrafluoroethylene and hexafluoropropylene) equipment under an atmosphere of dry argon.

4.1. Reaction of $C_6F_5BrF_2$ with $BF_3{\cdot}NCCH_3$ in CD_3CN/CD_2Cl_2

A solution of $BF_3{\cdot}NCCH_3$ (15 mg, 0.14 mmol) in CD_3CN (0.08 mL) was added to a cold (−78 °C) solution of $C_6F_5BrF_2$ (34 mg, 0.12 mmol) in CD_2Cl_2 (0.4 mL). The colorless solution (−82 °C) displayed ^{19}F NMR resonances at −128.5 (m, 2F, $F^{2,6}$), −135.4 (ttd, $^3J(F^4,F^{3,5}) = 22$ Hz, $^4J(F^4,F^{2,6}) = 9$ Hz, $^6J(F^4, BrF) = 9$ Hz, 1F F^4), −154.7 (m, 2F, $F^{3,5}$), −86.5 (s, $\tau_{1/2} = 30$ Hz, 1F, Br*F*) ppm, and the signal of $[BF_4]^-$ (δ −151.4 ppm) besides traces of $BF_3{\cdot}NCCH_3$ (δ −142.6 ppm) and C_6F_5Br. After warming to 20–22 °C, the brown solution showed signals of C_6F_5Br, **5**, and $[BF_4]^-$ (1:0.07:1.4).

4.2. Reaction of $C_6F_5BrF_2$ with BF_3 in SO_2ClF

A suspension of $C_6F_5BrF_2$ (37 mg, 0.13 mmol) in SO_2ClF (0.5 mL) was cooled to −30 °C and BF_3 was bubbled over a period of 5 min. The ^{19}F NMR spectrum of the colorless solution showed signals of **4**, **5**, 3-Br-1,4-C_6F_7 (**6**), and **7** (molar ratio 38:21:13:28).

4.3. Reaction of $C_6F_5BrF_2$ with aHF

Cold (−45 °C) aHF (0.2 mL) was added to cold (−45 °C) $C_6F_5BrF_2$ (**1**) (57 mg, 0.20 mmol). Immediately a white suspension was formed. The ^{19}F NMR spectrum (−40 °C) confirmed the absence of **1** in the mother liquor. The reaction mixture was warmed to 20 °C, mixed with CH_2Cl_2 and aHF was evaporated. The ^{19}F NMR spectrum of the dichloromethane solution contained resonances of **4**, **5**, 3-Br-1,4-C_6F_7 (**6**), and **7** (molar ratio 17:73:4:6). The same result was obtained when the reaction of **1** with aHF was performed at −80 °C.

4.4. Reaction of $C_6F_5IF_2$ with $BF_3{\cdot}NCCH_3$ in CD_3CN

A cold (−40 °C) solution of $BF_3{\cdot}NCCH_3$ (29 mg, 0.26 mmol) in CD_3CN (0.2 mL) was added to a cold (−40 °C) solution of $C_6F_5IF_2$ (66 mg, 0.20 mmol) in CD_3CN (0.3 mL). The colorless solution displayed unresolved ^{19}F NMR resonances at −119.9 (2F), −140.7 (1F), −155.9 (2F), and −191.2 (1F) ppm besides the signal of $[BF_4]^-$ (δ −147.6 ppm). The $^{13}C\{^{19}F\}$ NMR spectrum showed resonances at 147.7 (C-4), 146.5 (C-2,6), 138.7 (C-3,5), and 100.8 (C-1) ppm. No changes were detected after 4 h at −40 °C. When the solution was maintained at 20–22 °C for 17 h, it became brown and iodopentafluorobenzene appeared (molar ratio **2a**:**8** = 66:34) besides traces of IF_5 (^{19}F NMR). The measurement after 48 h displayed signals of C_6F_5I and $[BF_4]^-$ (1:1.4, molar) and IF_5 (trace).

4.5. Reaction of $C_6F_5IF_2$ with BF_3 in PFP

A. A solution of $C_6F_5IF_2$ (54 mg, 0.16 mmol) in PFP (0.7 mL) was cooled to −20 °C before BF_3 was bubbled over a period of 20 min to yield a yellow suspension. The ^{19}F NMR spectrum of the mother liquor showed a negligible amount of pentafluorophenyl compounds. The precipitate was separated by decantation and dried in vacuum at −20 °C to give a yellow product (46 mg). Its solution in cold (−40 °C) MeCN (0.5 mL) presented ^{19}F signals of $C_6F_5IF_2$, $[C_6F_5IF{\cdot}NCCH_3][BF_4]$, and $[(C_6F_5)_2I][BF_4]$ (molar ratio 47:42:11). Addition of mesitylene (0.11 mmol) and maintaining at 20 °C overnight resulted in $C_6F_5IF_2$, $[(2,4,6\text{-}C_6H_2(CH_3)_3)(C_6F_5)I][BF_4]$, C_6F_5I, and $[(C_6F_5)_2I][BF_4]$ (molar ratio 58:25:12:5) (^{19}F NMR).

B. Dissolution of the yellow precipitate (68 mg), which was obtained analogous from $C_6F_5IF_2$ (63 mg, 0.19 mmol) and BF_3 in PFP (0.5 mL), in cold (−20 °C) HF which contained water from exposure to air (0.5 mL) gave a colorless solution of $C_6F_5IF_2$ which contained $[BF_4]^-$ (2:1, molar) (^{19}F NMR).

4.6. *Reaction of $C_6F_5IF_2$ with BF_3 in CH_2Cl_2*

A FEP trap equipped with a magnetic stir bar was charged with $C_6F_5IF_2$ (165 mg, 0.50 mmol), CH_2Cl_2 (0.4 mL) and deposited in a stainless steel cylinder which was attached to a stainless steel vacuum line. After evacuation at −78 °C BF_3 (ca. 2 mmol) was filled in. The reaction mixture was stirred at −40 °C for 5 days. The excess of BF_3 was removed at −78 °C in vacuum (0.1 hPa) and the mother liquor was separated from the yellow precipitate after centrifugation at −78 °C. The precipitate was washed with cold (−40 °C) CH_2Cl_2 and dried in vacuum at −40 °C yielding a yellow solid (27 mg). The ^{19}F NMR spectrum of the latter in cold (−40 °C) MeCN showed resonances of $C_6F_5IF_2$, $[C_6F_5IF{\cdot}NCCH_3][BF_4]$, and $[(C_6F_5)_2I][BF_4]$ in a molar ratio of 26:53:21. The mother liquor contained $C_6F_5IF_2$ (^{19}F NMR).

4.7. *Reaction of $C_6F_5IF_2$ and $BF_3{\cdot}NCCH_3$ with mesitylene*

A solution of $[C_6F_5IF{\cdot}NCCH_3][BF_4]$ (0.28 mmol) obtained from equimolar amounts of $BF_3{\cdot}NCCH_3$ and $C_6F_5IF_2$ in MeCN (0.4 mL) at −40 °C was treated with a cold (−40 °C) solution of mesitylene (35 mg, 0.29 mmol) in CD_3CN (0.1 mL). After 1 h at −40 °C, volatiles were removed in vacuum, the residue was washed with CH_2Cl_2 (3× 0.2 mL) at 20 °C and dried in vacuum. Salt $[(2,4,6\text{-}C_6H_2(CH_3)_3)(C_6F_5)I][BF_4]$ was obtained in ca. 90% yield.

$[(2,4,6\text{-}C_6H_2(CH_3)_3)(C_6F_5)I][BF_4]$ (**14**). ^{1}H NMR (CD_3CN): $\delta = 7.26$ (m, 2H, $H^{3,5}$), 2.65 (s, 6H, $2CH_3$ ortho), 2.35 (s, 3H, CH_3 para). ^{19}F NMR (CD_3CN): $\delta = -120.9$ (m, 2F, $F^{2,6}$), −142.9 (tt, $^3J(F^4,F^{3,5}) = 20$ Hz,$^4J(F^4,F^{2,6}) = 6$ Hz, 1F, F^4), −155.8 (m, 2F, $F^{3,5}$), −149.2 (s, $[BF_4]^-$). ^{13}C NMR (CD_3CN): $\delta = 147.8$ (dm, $^1J(C,F) = 251$ Hz, C-2,6; C_6F_5), 146.6 (dtt, $^1J(C,F) = 260$ Hz, $^2J(C,F) = 13$ Hz, $^3J(C,F) = 5$ Hz, C-4; C_6F_5), 138.9 (dm, $^1J(C,F) = 259$ Hz, C-3,5; C_6F_5), 84.6 (td, $^2J(C,F) = 26$ Hz, $^4J(C,F) = 5$ Hz, C-1; C_6F_5), 146.8 (q, $^2J(C,H) = 6$ Hz, C-2′,6′; C_6H_2), 144.1 (m, C-4′; C_6H_2), 131.6 (dm, $^1J(C,H) = 165$ Hz, C-3′, 5′; C_6H_2), 121.9 (m, C-1′; C_6H_2), 27.0 (qm, $^1J(C,H) = 129$ Hz, *ortho*-CH_3), 21.0 (qtm, $^1J(C,H) = 128$ Hz, $^3J(C,H) = 4$ Hz, *para*-CH_3). **14** decomposed in a closed capillary at 161 °C. The products were dissolved in cold MeCN and gave C_6F_5I, $C_6H_2F(CH_3)_3$, and $BF_3{\cdot}NCMe$ in the molar ratio 1:1.1:1.2 (^{19}F NMR).

4.8. *Reaction of $C_6F_5IF_2$ with SbF_5 in SO_2ClF*

A solution of SbF_5 (144 mg, 0.66 mmol) in SO_2ClF (0.55 mL) was cooled to −20 °C and solid $C_6F_5IF_2$ (**2**) (84 mg, 0.25 mmol) was added in a one portion to form a deep green solution. The ^{19}F NMR at −20 °C revealed the formation of $[4\text{-I-}1,1,2,3,5,6\text{-}C_6F_6]^+$ (**2c**) (see Table 2), When the solution was kept at 20 °C for 1.5 h **2c** disappeared in the ^{19}F NMR and **9** and $[(C_6F_5)_2I]^+$ appeared. Subsequently the reaction mixture was cooled to −15 °C, diluted with aHF (0.1 mL) and poured onto ice which was treated with liquid nitrogen. The products were extracted with CH_2Cl_2 (1 mL). The ^{19}F NMR spectrum of the extract showed signals of C_6F_5I (**8**), $[(C_6F_5)_2I][F(HF)_n]$, 1-iodononafluorocyclohexene (**9**), 1-iodo-3-oxopentafluorocyclohexa-1,4-diene (**11**), and 1-iodo-6-oxopentafluorocyclohexa-1,4-diene (**12**) in the molar ratio 42:10:42:3:3 (overall yield ca. 72%) besides signals of secondary amounts of unknown compounds.

1-Iodo-3-oxopentafluorocyclohexa-1,4-diene (**11**). ^{19}F NMR (CH_2Cl_2): $\delta = -98.5$ (ddd, $^4J(F^6,F^2) = 10$ Hz, $^4J(F^6,F^4) = 10$ Hz, $^3J(F^6,F^5) = 25$ Hz, 2F, $F^{6,6}$), −103.3 (ddt, $^4J(F^2,F^4) = 3.5$ Hz, $^5J(F^2,F^5) = 4$ Hz, $^4J(F^2,F^6) = 10$ Hz, 1F, F^2), −135.6 (ddt, $^5J(F^5,F^2) = 3.5$ Hz, $^3J(F^5,F^4) = 5$ Hz, $^3J(F^5,F^6) = 25$ Hz, 1F, F^5), −152.9 (ddt, $^3J(F^4,F^5) = 4$ Hz, $^4J(F^4,F^2) = 4$ Hz, $^4J(F^4,F^6) = 10$ Hz, 1F, F^4).

1-Iodo-6-oxopentafluorocyclohexa-1,4-diene (**12**). ^{19}F NMR (CH_2Cl_2): $\delta = -90.9$ (ddt, $^4J(F^2,F^4) = 3$ Hz, $^5J(F^2,F^5) = 3$ Hz, $^3J(F^2,F^3) = 26$ Hz, 1F, F^2), −115.2 (ddd, $^4J(F^3,F^5) = 10$ Hz, $^3J(F^3,F^4) = 21$ Hz, $^3J(F^3,F^2) = 26$ Hz, 2F, $F^{3,3}$), −145.9 (ddt, $^5J(F^5,F^2) = 3$ Hz, $^3J(F^5,F^4) = 4$ Hz, $^4J(F^5,F^3) = 10$ Hz, 1F, F^5), −147.2 (ddt, $^3J(F^4,F^5) = 4$ Hz, $^4J(F^4,F^2) = 3$ Hz, $^3J(F^4,F^3) = 21$ Hz, 1F, F^4).

4.9. *Reaction of $C_6F_5IF_4$ with SbF_5 in SO_2ClF*

$C_6F_5IF_4$ (68 mg, 0.18 mmol) was added to the cold (−35 °C) solution of SbF_5 (158 mg, 0.73 mmol) in SO_2ClF (0.55 mL) in one portion to form a yellow solution. NMR measurements at ≤0 °C revealed the formation of **3d**. Following the solution was kept at 20 °C and became deep green within 20–30 min. After 2 h the green solution was cooled to −20 °C, diluted with aHF (0.1 mL) and poured onto ice which was treated with liquid nitrogen. Extraction with CH_2Cl_2 (1 mL) gave a solution of C_6F_5I, $[(C_6F_5)_2I][F(HF)_n]$, 1-iodononafluorocyclohexene (**9**), and iodoundecafluorocyclohexane (**10**) (molar ratio 53:4:26:17) (overall yield ca. 78%) besides traces of unknown non-aromatic compounds (^{19}F NMR).

Iodoundecafluorocyclohexane (**10**). ^{19}F NMR (CH_2Cl_2), δ: −104.8 (d, $^2J(F^{2a},F^{2e}) = 292$ Hz, 2F, $F^{2a,6a}$), −125.0 (d, $^2J(F^{2e},F^{2a}) = 292$ Hz, 2F, $F^{2e,6e}$), −121.8 (d, $^2J(F^{3a},F^{3e}) = 289$ Hz, 2F, $F^{3a,5a}$), −135.6 (d, $^2J(F^{3e},F^{3a}) = 285$ Hz, 2F, F^{3e},F^{5e}), −122.8 (d, $^2J(F^{4a},F^{4e}) = 285$ Hz, 1F, F^{4a}), −141.8 (d, $^2J(F^{4e},F^{4a}) = 285$ Hz, 1F, F^{4e}), −144.6 (m, 1F, F^1) ppm (cf. [34]).

4.10. *Reaction of C_6F_5I with SbF_5 in SO_2ClF*

A. C_6F_5I (38 mg, 0.13 mmol) was added in one portion to the cold solution (−50 °C) of SbF_5 (96 mg, 0.44 mmol) in SO_2ClF (0.55 mL) to give a deep blue solution. The ^{19}F NMR spectrum (−30 °C) showed only resonances at 99.8 ppm (SO_2ClF) and broad resonances at −86 and −123 ppm (Sb^V–F). Warming to 20 °C caused the formation of a deep green solution. After 1.5 h at 20 °C, the ^{19}F NMR signals of the cation $[(C_6F_5)_2I]^+$ ($\delta = -117.7$ ($F^{2,6}$), −133.8 (F^4), and −151.2 ($F^{3,5}$) ppm) were observed in addition to the above-mentioned resonances. The solution was kept at 20 °C overnight, cooled to −10 °C, diluted with aHF (0.2 mL) and poured onto ice which was treated with liquid nitrogen. After melting of the ice, the products were extracted with CH_2Cl_2 (1 mL). The extract contained C_6F_5I and $[(C_6F_5)_2I][F(HF)_n]$ (74:26) (^{19}F NMR).

B. When the deep green solution of C_6F_5I (187 mg, 0.63 mmol) and SbF_5 (419 mg, 1.93 mmol) in SO_2ClF (0.5 mL) was kept at 22 °C over a period of 5 days a dark precipitate formed. The reaction mixture was cooled to 0 °C and poured onto ice treated with liquid nitrogen. After melting of the ice, the brown suspension was extracted with pentane (1 mL). The rose extract showed signals of C_6F_5I (0.24 mmol) (^{19}F NMR). The aqueous phase was saturated with $Na[BF_4]$ and $[(C_6F_5)_2I][BF_4]$ (84 mg, 0.15 mmol) was filtered off.

4.11. Reaction of $C_6F_{13}IF_4$ with AsF_5 in CCl_3F

The solution of $C_6F_{13}IF_4$ (0.15 mmol) in CCl_3F (0.5 mL) was cooled to −60 °C and AsF_5 (ca. 1 mmol) was condensed. Immediately a dark precipitate formed. After 10 min the temperature was raised to −40 °C and the excess of AsF_5 was removed under a stream of dry argon. The ^{19}F NMR spectrum (−40 °C) showed signals of C_6F_{14} at −81.4, −123.5, and −127.0 ppm (yield 90%) besides resonances of CCl_3F and residual AsF_5 (−59 ppm, broad).

4.12. Solution of $[IF_4][SbF_6]$ in SO_2ClF

The salt $[IF_4][SbF_6]$ [35] (43 mg, 0.1 mmol) was cooled to −15 °C and SO_2ClF (0.5 mL) was condensed to yield a colorless solution. The ^{19}F NMR spectrum contained resonances at 21.8 (s $[IF_4]^+$) and −109 ppm (br, s, $[SbF_6]^-$) and did not change in the temperature range from −40 to −10 °C.

5. Conclusions

The relative fluoride donor ability decreased in order $C_6F_5BrF_2 > C_6F_5IF_2 > C_6F_5IF_4$. In contrast to the stability of di(organyl)iodonium and di(organyl)bromonium salts, salts with the cations $[C_6F_5HalF]^+$, generated by fluorine abstraction from $C_6F_5HalF_2$, are highly unstable. They were detected as solvates $[C_6F_5HalF\cdot(NCCH_3)_n][BF_4]$ in basic acetonitrile. In aHF (Hal = Br) or in weakly coordinating solvents, the pentafluorophenyl(fluoro)halonium cations $[C_6F_5HalF]^+$ converted spontaneously via halohexafluorobenzenium cations into C_6F_5Hal and 1-X-nonafluorocyclohexene (and bromoheptafluorocyclohexa-1,4-dienes when Hal = Br). Aryl(trifluoro)iodonium fluoroantimonates $[ArIF_3][Sb_nF_{5n+1}]$ (Ar = C_6H_5 [19], C_6F_5 ([18] and present work)) are more stable salts. Decomposition of $[C_6F_5IF_3][SbF_6]$ in SO_2ClF at 20 °C resulted in C_6F_5I, 1-I-*cyclo*-C_6F_9, and *cyclo*-$C_6F_{11}I$.

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