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Explored routes to unknown polyfluoroorganyliodine hexafluorides, R_FIF_6

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ABSTRACT

Two routes to R_FIF_6 compounds were investigated: (a) the substitution of F by R_F in IF_7 and (b) the fluorine addition to iodine in R_FIF_4 precursors. For route (a) the reagents $C_6F_5SiMe_3$, $C_6F_5SiF_3$, $[NMe_4][C_6F_5SiF_4]$, $C_6F_5BF_2$, and 1,4-$C_6F_4(BF_2)_2$ were tested. $C_6F_5IF_4$ and $CF_3CH_2IF_4$ were used in route (b) and treated with the fluoro-oxidizers IF_7, $[O_2][SbF_6]$/KF, and $K_2[NiF_6]$/KF. The observed sidestep reactions in case of routes (a) and (b) are discussed. Interaction of $C_6F_5SiX_3$ (X = Me, F), $C_6F_5BF_2$, 1,4-$C_6F_4(BF_2)_2$ with IF_7 gave exclusively the corresponding ring fluorination products, perfluorinated cyclohexadiene and cyclohexene derivatives, whereas $[NMe_4][C_6F_5SiF_4]$ and IF_7 formed mixtures of $C_6F_nIF_4$ and C_6F_nH compounds (n = 7 and 9). $CF_3CH_2IF_4$ was not reactive towards the fluoro-oxidizer IF_7, whereas $C_6F_5IF_4$ formed $C_6F_nIF_4$ compounds (n = 7 and 9). $C_6F_5IF_4$ and $CF_3CH_2IF_4$ were inert towards $[O_2][SbF_6]$ in anhydrous HF. $CF_3CH_2IF_4$ underwent C–H fluorination and C–I bond cleavage when treated with $K_2[NiF_6]$/KF in HF. The fluorine addition property of IF_7 was independently demonstrated in case of perfluorohexenes. $C_4F_9CF{=}CF_2$ and IF_7 underwent oxidative fluorine addition at −30 °C, and the isomers $(CF_3)_2CFCF{=}CFCF_3$ (*cis* and *trans*) formed very slowly perfluoroisohexanes even at 25 °C. The compatibility of IF_7 and selected organic solvents was investigated. The polyfluoroalkanes $CF_3CH_2CHF_2$ (PFP), $CF_3CH_2CF_2CH_3$ (PFB), and C_4F_9Br are inert towards iodine heptafluoride at 25 °C while CF_3CH_2Br was slowly converted to CF_3CH_2F. Especially PFP and PFB are new suitable organic solvents for IF_7.

1. Introduction

Iodine heptafluoride belongs to the rare types of molecules with a hepta-coordinated central atom. For the first time, it was prepared by Ruff and Keim from the elements in 1930 [1]. Up to date its reactivity is not studied comprehensively. In 1989 some chemical, physical, and spectral (NMR, Raman, IR) data of IF_7 were briefly reviewed [2]. Furthermore fluoride donor/acceptor properties [3–5], the hydrolysis, and fluorine–oxygen substitution reactions with MNO_3 [3] were reported. The structural data of IF_7 were discussed in [6,7]. To our knowledge, the reactivity of IF_7 towards organo compounds and the substitution of fluorine by organyl groups were not investigated.

In the present paper we show the compatibility of selected polyfluorinated alkanes towards iodine heptafluoride and their potential as solvents for IF_7. We report results of the attempted syntheses of the hitherto unknown type of R_FIF_6 molecules by two different reaction routes: (a) by F/R_F substitution in IF_7 and (b) by fluorine addition to iodine in R_FIF_4 precursors with different fluoro-oxidizers.

2. Results and discussion

2.1. Suitable organic solvents for IF_7 and compatibility of selected polyfluoroalkanes towards IF_7

Iodine heptafluoride is well soluble in 1,1,1,3,3-pentafluoropropane (HFC-245fa) (PFP) (>1.3 mmol or >340 mg per mL at −70 °C) as well in 1,1,1,3,3-pentafluorobutane (Solkane® 365mfc) (PFB). The colorless solutions could be stored in FEP traps at 25 °C over 40 h without any attack on the polyfluoroalkanes. The inertness towards strong fluoro-oxidizers combined with a wide range of the liquid state of PFB (mp −36 °C, bp 40 °C) and PFP (mp −103 °C, bp 15 °C) and a good solubility of many polyfluoroorgano compounds suggest the use of both polyfluoroalkanes as solvents for investigations of the reactivity of IF_7. The content of IF_7 in solution was controlled by ^{19}F NMR spectrometry at low temperature. The ^{19}F NMR spectrum of IF_7 in PFP displayed a resonance at 171 ppm which showed a temperature-depending reversible broadening from $\Delta\nu_{1/2}$ = 1180 Hz (−90 °C) to 1480 Hz (−70 °C), 5200 Hz (−40 °C), and 6700 Hz (0 °C). These data coincide with the reported spectra of IF_7 in CCl_3F (δ(F) = 173.5, $\Delta\nu_{1/2}$ = 1150 Hz at −110 °C) [7] and of neat liquid IF_7 (δ(F) = 171, $\Delta\nu_{1/2}$ = 4100 ± 300 Hz at 27 °C) [8].

Iodine heptafluoride did also not react with C_4F_9Br in PFP (25 °C, 24 h) and reacted very slowly with CF_3CH_2Br, where bromine

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carries more partial negative charge, to give CF_3CH_2F (trace after 27 h at 25 °C). After 60 h at 25 °C the quantitative reduction of IF_7 to IF_5 and the formation of polyfluoroethanes CF_3CH_2F and CF_3CHF_2 were observed.

2.2. Attempts to synthesize R_FIF_6 by F/R_F substitution in IF_7

From our previous systematic investigations of F/R_F substitution reactions in halogen fluorides it was known that BrF_3 [9] and BrF_5 [10] reacted with $C_6F_5SiMe_3$ in CH_2Cl_2 in the presence of the base MeCN to give $C_6F_5BrF_n$ (n = 2, 4). Under similar conditions IF_3 [9] and IF_5 [11] showed no substitution. We have now found that the addition of a pentafluorophenyltrimethylsilane (**1**) – MeCN (1:3) solution in PFP to a solution of IF_7 in PFP at −60 to −40 °C led to the slow reduction of IF_7 to IF_5 and fluorine addition to the pentafluorophenyl moiety giving heptafluorocyclohexa-1,4-dien-1-yltrimethylsilane (**2**), nonafluorocyclohex-1-en-1-yltrimethylsilane (**3**), nonafluorocyclohex-1-en-3-yltrimethylsilane (**4**), nonafluorocyclohex-1-en-4-yltrimethylsilane (**5**), octafluorocyclohexa-1,4-diene (**6**), and decafluorocyclohex-1-ene (**7**), besides a trace of Me_3SiF (Scheme 1).

Pentafluorophenyltrifluorosilane (**8**) was a successful reagent for F/C_6F_5 mono-substitution in IF_3 [9], IF_5 [11], BrF_3 [12], and BrF_5 [13] under formation of $C_6F_5HalF_{n-1}$ (n = 3, 5). In case of BrF_3 we were able to show that **8** can also form the di-substitution product $[(C_6F_5)_2Br]^+$ in reactions with a 1:2 ratio at elevated temperatures [14].

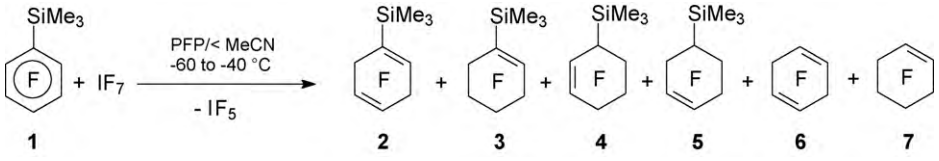
Stirring pentafluorophenyltrifluorosilane (**8**), MeCN, and iodine heptafluoride (1:2:0.8) in a PFP solution at −70 to −40 °C for 1.5 h did not lead to $C_6F_5IF_6$. Instead, a mixture of IF_7 and IF_5 (1:2) together with heptafluorocyclohexa-1,3-dien-1-yltrifluorosilane (**9**), heptafluorocyclohexa-1,4-dien-1-yltrifluorosilane (**10**), nonafluorocyclohex-1-en-1-trifluorosilane (**11**), 1-H-heptafluorocyclohexa-1,4-diene (**12**), perfluorinated cycloalkenes **6**, **7**, and SiF_4 was formed. Warming up to 0 °C resulted in the complete consumption of IF_7 (Scheme 2). The predominant reactivity of IF_7 was again fluorine addition across the C=C double bonds of the phenyl group.

Iodine heptafluoride and a suspension of $[Me_4N][C_6F_5SiF_4]$ in PFP reacted at −30 to 0 °C under fluorine addition to the aromatic ring too, but the perfluorinated cycloalkenyltrifluorosilanes **9**, **10**, and **11** were not formed. Instead, the perfluorocycloalkenyliodine tetrafluorides **14** and **15** were found together with 1-H-polyfluorocycloalkenes **12** and **13**, the perfluorinated cycloalkenes **6** and **7**, and iodine pentafluoride (Scheme 3).

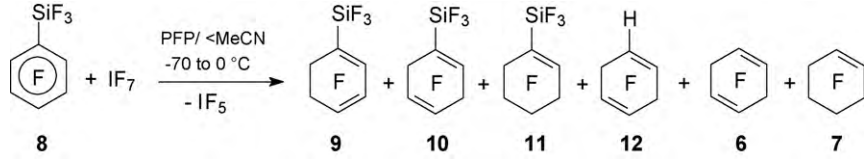
Principally, the formation of **14** and **15** from $C_6F_5IF_6$ cannot be excluded, but it seems more likely that they were formed by alternative routes. Thus, the fluorination of $[C_6F_5SiF_4]^-$ by IF_7 led to $[cyclo\text{-}C_6F_nSiF_4]^-$ (n = 7, 9) and IF_5. IF_5 can then react by two channels. IF_5 and $[C_6F_5SiF_4]^-$ give $C_6F_5IF_4$ [15] which can be fluorinated by IF_7 (see below) to **14** and **15** (Scheme 7). Alternatively, compounds **14** and **15** can be produced from $[cyclo\text{-}C_6F_nSiF_4]^-$ and IF_5. The remarkable quantity of hydrogen-containing cycloalkenes **12** and **13** is explained by a transformation of **14** and **15** under the influence of fluoride ions [16].

During the last decade we have successfully used pentafluorophenyldifluoroborane (**16**) as a pentafluorophenyl transfer reagent for the preparation of pentafluorophenyliodonium(III, V), pentafluorophenylbromonium(III) [17,18,14], and pentafluorophenylxenonium(II, IV) [19] salts. Based on this experience borane **16** seemed to offer a promising route to first types of up to now unknown organyliodine(VII) compounds. Thus we studied the reaction of **16** with iodine heptafluoride. We have found that after addition of **16** in PFP to an equimolar amount of IF_7 in PFP at −60 °C only ring fluorination resulted and no hint on $C_6F_5IF_6$ was obtained (Scheme 4). Besides IF_5, heptafluorocyclohexa-1,3-dien-1-yldifluoroborane (**17**), heptafluorocyclohexa-1,4-dien-1-yldifluoroborane (**18**), and nonafluorocyclohex-1-en-1-yldifluoroborane (**19**), in addition to a significant amount of BF_3, the perfluorinated diene **6** and alkene **7** were formed. In contrast to the reaction with $[C_6F_5SiF_4]^-$, perfluorocycloalkenyliodine tetrafluorides **20**, **14**, and **15** were not found in the reaction solution after several days at 25 °C. This fact allows to conclude that no slow substitution of the BF_2 group by IF_4 proceeded as consecutive reaction between perfluoroalkenyl(difluoro)boranes and IF_5.

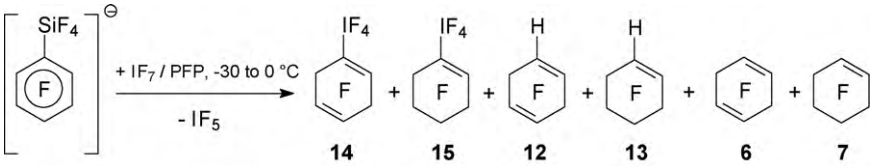
To reduce the probability of fluorine addition to the aromatic moiety, we included tetrafluorophenylen-1,4-bis(difluoroborane) (**21**) in our F/R_F investigations. Borane **21** contains two strong electron-withdrawing BF_2 groups ($\sigma_I(BF_2)$ = 0.15, $\sigma_R(BF_2)$ = 0.30



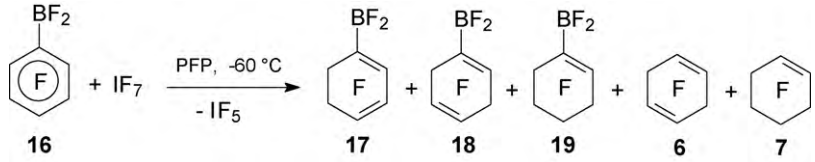
Scheme 1.



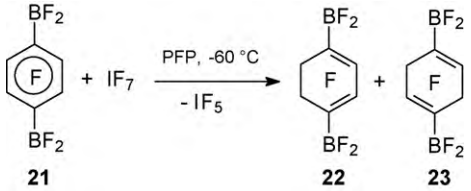
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

[20]). Nevertheless, after addition of an equimolar amount of **21** to IF_7 in PFP at −60 °C we have found again fluorine addition to the double bonds instead of F/R_F substitution. Hexafluorocyclohexa-1,3-dienylen-1,4-bis(difluoroborane) (**22**) and hexafluorocyclohexa-1,4-dienylen-1,4-bis(difluoroborane) (**23**) were formed in quantitative yields (Scheme 5).

Under the action of a second equivalent of IF_7, the conjugated isomer **22** was converted into cycloalkenyldifluoroborane **19**, cycloalkene **7**, and boron trifluoride (Scheme 6).

When the reaction solution was kept at 25 °C over a period of 4 days, 1,4-diene **23** isomerized to 1,3-diene **22**.

Why did the pentafluorophenyl transfer not proceed in IF_7? The experimental facts with IF_7 argue for a fast fluorine addition to the aryl-transfer reagent and a low rate for the F/C_6F_5 substitution in IF_7. Indeed, we can deduce a slow F/C_6F_5 substitution in IF_7 relative to iodine(III) and iodine(V) fluorides based on the following examples. The rate of F/C_6F_5 substitution in $C_6F_5IF_n$ with $C_6F_5BF_2$ in CH_2Cl_2 decreases from $n = 2$ [21] to $n = 4$ [22] (Eqs. (1) and (2)).

$$C_6F_5IF_2 + C_6F_5BF_2 \xrightarrow[20\,^\circ C,\ 0.5\,h]{CH_2Cl_2} \underset{93\%}{[(C_6F_5)_2I][BF_4]} \quad (1)$$

$$C_6F_5IF_4 + C_6F_5BF_2 \xrightarrow[16-20\,^\circ C,\ 70\,h]{CH_2Cl_2} \underset{64\%}{[(C_6F_5)_2IF_2][BF_4]} \quad (2)$$

A similar trend was observed for the F/C_6F_5 substitution in BrF_3, BrF_5, and IF_5 in reactions with silane **8**. The reaction of BrF_3 with $C_6F_5SiF_3$ in CCl_3F was completed within 1 h [12] (Eq. (3)) whereas the aryl transfer to BrF_5 required the presence of MeCN and occurred within 12 h [10,13] (Eq. (4)). The related reaction of IF_5 needed the presence of the stronger base pyridine and more rigid conditions [11] (Eq. (5)).

$$C_6F_5SiF_3 + BrF_3 \xrightarrow[-5\ to\ 0\,^\circ C,\ <1\,h]{CCl_3F} \underset{47\%}{C_6F_5BrF_2} + SiF_4 \quad (3)$$

$$C_6F_5SiF_3 + BrF_5 \xrightarrow[0\,^\circ C,\ 12\,h]{CClF_2CClF_2,\ 4MeCN} \underset{58\%}{C_6F_5BrF_4} + SiF_4 \cdot 2MeCN \quad (4)$$

$$C_6F_5SiF_3 + IF_5 + 2Py \xrightarrow[20\,^\circ C,\ 24\,h]{MeCN} \underset{100\%}{C_6F_5IF_4} + SiF_4 \cdot 2Py \quad (5)$$

2.3. Attempts to synthesize R_FIF_6 by fluorination of iodine in R_FIF_4 precursors

We have included $C_6F_5IF_4$ and $CF_3CH_2IF_4$ in reactions with fluoro-oxidizers with the aim to obtain the corresponding R_FIF_6 molecules. The treatment of pentafluorophenyliodine tetrafluoride (**24**) with IF_7 (1 equiv.) in PFP at −60 to −30 °C did not result in $C_6F_5IF_6$ but fluorine addition across C=C bonds occurred under formation of heptafluorocyclohexa-1,3-dien-1-yliodine tetrafluoride (**20**), heptafluorocyclohexa-1,4-dien-1-yliodine tetrafluoride (**14**), and nonafluorocyclohex-1-en-1-yliodine tetrafluoride (**15**) (Scheme 7).

A similar ring fluorination of **24** was observed with XeF_2 in the presence of a Lewis acid [23]. Both results indicate (a) that the electron-withdrawing effect of the IF_4 group is not strong enough to protect the C_6F_5 group against such strong fluoro-oxidizers or (b) that the valence electron lone pair of iodine(V) needs a stronger fluoro-oxidizer. If conclusion (b) is true, then this route can be excluded for R_FIF_6 syntheses where R_F contains a C–C multiple bond.

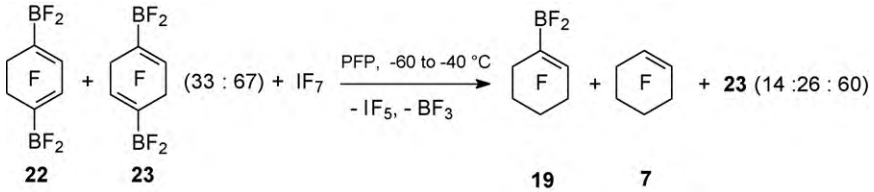
In order to evaluate the influence of the oxidation number of iodine on the preference of channel (a) or (b) in C_6F_5I starting materials we performed the reaction of iodopentafluorobenzene (**25**) (1.6 equiv.) with IF_7 and observed 57% conversion of C_6F_5I to pentafluorophenyliodine difluoride (**26**) and IF_5 (Eq. (6)). No addition of fluorine to the C=C double bond took place.

$$\underset{\mathbf{25}}{C_6F_5I} + {<}1IF_7 \xrightarrow{PFP,\ -40\ to\ 0\,^\circ C} \underset{\mathbf{26}}{C_6F_5IF_2} + IF_5 \quad (6)$$

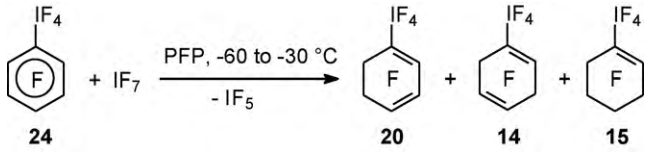
In order to avoid the reaction channel of fluorine addition to C=C bonds we investigated the reaction of $CF_3CH_2IF_4$ with IF_7. We have found that IF_7 and 2,2,2-trifluoroethyliodine tetrafluoride (**27**) did not react in PFP even at 25 °C over 16 h (Eq. (7)). The unexpected inertness of $CF_3CH_2IF_4$ prompted us to exclude perfluoroalkyliodine tetrafluorides with a more electron-deficient iodine atom from our investigations with IF_7.

$$\underset{\mathbf{27}}{CF_3CH_2IF_4} + IF_7 \xrightarrow{PFP,\ 25\,^\circ C,\ 16\,h} \text{no reaction} \quad (7)$$

In addition to the fluoro-oxidizer IF_7 we investigated selected reactions with $[O_2][SbF_6]$ and $K_2[NiF_6]$ under different conditions. $C_6F_5IF_4$ showed no reactivity towards $[O_2][SbF_6]$ in aHF till 0 °C (Eq. (8)). The inertness of $C_6F_5IF_4$ towards the one-electron-oxidizer



Scheme 6.



Scheme 7.

$$CF_3CH_2IF_4 + K_2[NiF_6] + KF \xrightarrow{\text{aHF, 0 °C}} CF_3CH_2F + CF_3CHF_2 + IF_5$$

Scheme 8.

$[O_2]^+$ is in contrast to the easy oxidation of the parent aryl compound C_6F_6 under formation of the radical cation $[C_6F_6]^{+\bullet}$ [24].

$$C_6F_5IF_4 + 2[O_2][SbF_6] \xrightarrow{\text{aHF},\leq 0\,^\circ C} \text{no reaction} \quad (8)$$

From the work of Bartlett [25] it was known that $[O_2][SbF_6]$ dissolved in "basic" aHF below −50 °C provides the strong radical fluoro-oxidizer O_2F with an O–F bond energy of ~13 kcal/mol. When we treated $CF_3CH_2IF_4$ with $[O_2][SbF_6]$/KF/aHF from −65 to 24 °C no reaction proceeded (Eq. (9)).

$$CF_3CH_2IF_4 + 2[O_2][SbF_6] + 2KF \xrightarrow{\text{aHF},-65 \text{ to } 24\,^\circ C} \text{no reaction} \quad (9)$$

The same combination of reagents converted CF_3CH_2I at −65 to 0 °C partially into $CF_3CH_2IF_4$ (Eq. (10)).

$$CF_3CH_2I + 5[O_2][SbF_6] + > 5KF \xrightarrow[\text{partial conversion}]{\text{aHF},-65 \text{ to } 0\,^\circ C} CF_3CH_2IF_4 + 5O_2 + 5K[SbF_6] \quad (10)$$

Finally, we reacted $CF_3CH_2IF_4$ with $K_2[NiF_6]$ in "basic" aHF. At 0 °C we observed the splitting of the C–I bond by fluorination and formation of CF_3CH_2F and IF_5. In a smaller extent also one C–H bond was fluorinated (formation of CF_3CHF_2) (Scheme 8).

2.4. Verification of the fluorine addition property of IF_7 exemplified by using a "non" polarized C=C double bond

All aforementioned fluorine additions to the C_6F_5 moiety were influenced by the substituent at carbon-1: SiF_3, BF_2, IF_4 groups as electron-withdrawing substituents or $SiMe_3$ and SiF_4^- as electron-pushing substituents. We have chosen two constitutional isomers of perfluorohexene in order to test the fluorine addition property of IF_7 to a "non" polarized C=C bond.

No reaction between iodine heptafluoride and perfluorohex-1-ene (**28**) was detected in PFP at −60 °C within 2 h, but at −30 °C fluorine addition across the terminal C=C bond took place forming perfluorohexane (**29**) (Eq. (11)). Under the same conditions, the isomer perfluoro-4-methylpent-2-ene (**31**) with an internal C=C bond was not fluorinated by IF_7. A slow conversion of both *cis*-**31** and *trans*-**31** to perfluoroisohexane (**33**) proceeded at 24 °C and was completed after 60 h (Eq. (12)). It is noteworthy that during the long-term reaction in a FEP trap the fluorine addition was accompanied by the formation of minor by-products $(CF_3)_2CFCOF$, CF_3COF (derived from **31**) and $(CF_3)_2CO$ and C_2F_5COF (derived from the isomer $(CF_3)_2C{=}CFC_2F_5$). Probably, the slow formation of oxygen-containing products was caused by water vapor which diffused through the 0.35 mm fluoropolymer wall.

$$\underset{\mathbf{28}}{C_4F_9CF_2{=}CF_2} + IF_7 \xrightarrow{\text{PFP},-30\,^\circ C,\ 2\,h} \underset{\mathbf{29}}{C_6F_{14}} + IF_5 \quad (11)$$

$$\underset{\mathbf{31}(cis:trans=12.88)}{(CF_3)_2CFCF{=}CFCF_3} + IF_7 \xrightarrow{\text{PFP},\ 24\,^\circ C,\ 60\,h} \underset{\mathbf{33}}{(CF_3)_2CFC_3F_7} + IF_5 \quad (12)$$

3. Experimental

3.1. General

The NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (300.13 MHz, ^1H; 282.40 MHz, ^{19}F; 96.29 MHz, ^{11}B; 75.47 MHz, ^{13}C). The chemical shifts are referenced to TMS (^1H, ^{13}C), $BF_3{\cdot}OEt_2/CDCl_3$ (15%, v/v) (^{11}B), and CCl_3F (^{19}F, with C_6F_6 as secondary reference (−162.9 ppm)), respectively. The composition of reaction mixtures and the yields of products were determined by ^{19}F NMR spectroscopy using the internal integral standards C_6F_6, C_4F_9Br, or PFB.

Products *cyclo*-1,3-C_6F_7-1-IF_4 (**20**), *cyclo*-1,4-C_6F_7-1-IF_4 (**14**), and *cyclo*-1-C_6F_9-1-IF_4 (**15**) [23], *cyclo*-1,3-C_6F_7-1-SiF_3 (**9**), *cyclo*-1,4-C_6F_7-1-SiF_3 (**10**), *cyclo*-1,4-C_6F_7-1-$SiMe_3$ (**2**), *cyclo*-1-C_6F_9-1-SiF_3 (**11**), *cyclo*-1-H-1,4-C_6F_7 (**12**), *cyclo*-1,4-C_6F_8 (**6**), [26], *cyclo*-1-C_6F_9-1-$SiMe_3$ (**3**) [27], and *cyclo*-1-H-1-C_6F_9 (**13**) [28] were identified by ^{19}F NMR spectroscopy.

1,1,1,3,3-Pentafluoropropane (PFP) (Honeywell), 1,1,1,3,3-pentafluorobutane (PFB) (Solvay), and CCl_3F (K11, Solvay) were stored over molecular sieves 3 Å before use. Boron trifluoride (Air Liquide), C_6F_5I (Bristol Organics), CF_3CH_2I (**30**) (Acros), $(CF_3)_2CFCF{=}CFCF_3$ (**31**) (ABCR) were used as supplied. Acetonitrile (Baker) and dichloromethane (Baker) were purified and dried as described in Ref. [29]. Anhydrous HF (aHF) was stored over CoF_3. Compounds CF_3CH_2Br (**32**) [30], $C_4F_9CF{=}CF_2$ [31], $C_6F_5SiF_3$ (**8**) [32], $C_6F_5SiMe_3$ (**1**) [33], $C_6F_5IF_4$ (**24**) [34], $[Me_4N]F$ [35], PFP solutions of $C_6F_5BF_2$ [18] and of 1,4-$C_6F_4(BF_2)_2$ [36] were prepared as described. IF_7 was obtained from E. Jacob and stored in a Monel cylinder with a Monel valve, $[O_2][SbF_6]$ from B. Müller, and $K_2[NiF_6]{\cdot}KF$ from H. Willner.

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

3.2. Preparation of $CF_3CH_2IF_4$

(A) Xenon difluoride (352 mg, 2.08 mmol), PFB (2 mL) and CF_3CH_2I (200 mg, 0.95 mmol) were loaded in a 11.7-mm i.d. PFA trap equipped with a magnetic stir bar. The solution was cooled to −10 °C and BF_3 was bubbled under stirring at −10 °C for 2 min and at 20 °C for 40 min. The ^{19}F NMR spectrum showed the formation of $CF_3CH_2IF_4$. The signals of XeF_2 and CF_3CH_2I were absent. Volatiles were evaporated at 20 °C under reduced pressure to give $CF_3CH_2IF_4$ (216 mg, 0.76 mmol, 79%) (white solid).

(B) CF_3CH_2I (117 mg, 0.55 mmol) and aHF (2 mL) were loaded in a 11.7-mm i.d. PFA trap equipped with a magnetic stir bar. The emulsion was cooled to 0 °C before a solution of XeF_2 (233 mg, 1.37 mmol) in aHF (0.5 mL) was added in portions. The mixture was stirred at 10–12 °C for 15 min and the excess of XeF_2 was quenched by the addition of C_6F_6. All volatiles were removed at 20 °C in vacuum. The residue was washed with pentane and dried in vacuum to give $CF_3CH_2IF_4$ in >90% yield.

$CF_3CH_2IF_4$. ^1H NMR (PFB, 24 °C): δ 4.86 (q $^3J(H^1, F^2)$ = 9 Hz, 2H, H^1). ^1H NMR (aHF, 0 °C): δ 4.90 (q $^3J(H^1, F^2)$ = 9 Hz, 2H, H^1). ^{19}F NMR (PFP, 24 °C): δ −19.9 (t $^3J(IF_4, H^1)$ = 5 Hz, q $^4J(IF_4, F^2)$ = 9 Hz, 4F, IF_4), −59.6 (t $^3J(F^2, H^1)$ = 9 Hz, quin $^4J(F^2, IF_4)$ = 9 Hz, 3F, F^2). ^{19}F NMR (aHF, 0 °C): δ −23.2 (s, $\Delta\nu_{1/2}$ = 47 Hz, 4F, IF_4), −58.6 (t $^3J(F^2, H^1)$ = 9 Hz, 3F, F^2). $^{13}C\{^{19}F\}$ NMR (PFB, 24 °C): δ 121.0 (t ^2J(C-2, H^1) = 6 Hz, C-2), 75.4 (t ^1J(C-1, H^1) = 152 Hz, C-1).

3.3. Reaction of IF_7 with 2-bromo-1,1,1-trifluoroethane

A cold (−65 °C) solution of CF_3CH_2Br (0.10 mmol) in PFP (0.15 mL) was added to a cold (−65 °C) solution of IF_7 (0.10 mmol)

in PFP (0.30 mL). The solution was stirred at −60 °C for 2 h, at 25 °C for 16 h (without reaction, ^{19}F NMR) and for additional 27 h (trace of CF_3CH_2F). After 60 h at 25 °C the red solution contained IF_5 (0.10 mmol), CF_3CH_2Br (0.01 mmol), CF_3CH_2F (0.08 mmol), and CF_3CHF_2 (0.01 mmol) (PFB as internal integral standard, ^{19}F NMR).

3.4. Attempts to substitute fluorine by pentafluorophenyl groups in IF_7

3.4.1. Reaction of IF_7 with pentafluorophenyltrimethylsilane

Cold (−45 °C) solutions of CH_3CN (15 mg, 0.36 mmol) and $C_6F_5SiMe_3$ (**1**) (29 mg, 0.12 mmol) in PFP (each 0.4 mL) were added to a cold (−70 °C) solution of IF_7 (0.10 mmol) in PFP (0.25 mL). The solution was stirred for 0.5 h at −60 °C and at −40 °C. The ^{19}F NMR spectrum (−40 °C) showed signals of IF_7 (too broad for integration), IF_5, **2**, **3**, **6**, **7**, **4**, **5** (189:45:17:2:4:15:21) and Me_3SiF (trace). Stirring at 0–6 °C for 13 h led to the complete reduction of IF_7 to IF_5 and the corresponding changes in the molar ratio of products: IF_5, **2**, **3**, **6**, **7**, **4**, **5**, and Me_3SiF (217:26:22:3:4:15:29:8).

cyclo-1-C_6F_9-3-$SiMe_3$ (**4**). ^{19}F NMR (PFP): δ −109.8 (d $^2J(F^{6A}, F^{6B})$ = 280 Hz, 1F, F^{6A}), −115.2 (d $^2J(F^{6B}, F^{6A})$ = 280 Hz, 1F, F^{6B}), −122.4 (d $^2J(F^{4A}, F^{4B})$ = 270 Hz, 1F, F^{4A}), −141.2 (d $^2J(F^{4B}, F^{4A})$ = 270 Hz, 1F, F^{4B}), −126.7 (d $^2J(F^{5A}, F^{5B})$ = 280 Hz, 1F, F^{5A}), −128.0 (d $^2J(F^{5B}, F^{5A})$ = 280 Hz, 1F, F^{5B}), −129.0 (d $^3J(F^2, F^1)$ = 9 Hz, d $^4J(F^2, F^{6A})$ = 12 Hz, d $^3J(F^2, F^3)$ = 32 Hz, 1F, F^2), −155.4 (d $^3J(F^1, F^2)$ = 9 Hz, d $^4J(F^1, F^3)$ = 12 Hz, t $^3J(F^1, F^{6A,6B})$ = 19 Hz, 1F, F^1), −186.8 (m, d $^4J(F^3, F^1)$ = 12 Hz, d $^3J(F^3, F^2)$ = 32 Hz, 1F, F^3).

cyclo-1-C_6F_9-4-$SiMe_3$ (**5**). ^{19}F NMR (PFP): δ −105.8 (d $^2J(F^{6A}, F^{6B})$ = 282 Hz, 1F, F^{6A}), −126.1 (m, d $^2J(F^{6B}, F^{6A})$ = 282 Hz, d $^4J(F^{6B}, F^2)$ = 15 Hz, d $^3J(F^{6B}, F^1)$ = 28 Hz, 1F, F^{6B}), −99.7 (d $^2J(F^{3A}, F^{3B})$ = 303 Hz, 1F, F^{3A}), −110.2 (d $^2J(F^{3B}, F^{3A})$ = 303 Hz, 1F, F^{3B}), −112.5 (m, d $^2J(F^{5A}, F^{5B})$ = 288 Hz, 1F, F^{5A}), −124.3 (m, d $^2J(F^{5B}, F^{5A})$ = 288 Hz, 1F, F^{5B}), −151.8 (m, d $^4J(F^2, F^{6A})$ = 9.5 Hz, d $^4J(F^2, F^{6B})$ = 15 Hz, d $^3J(F^2, F^{3A})$ = 20 Hz, d $^3J(F^2, F^{3B})$ = 24 Hz, 1F, F^2), −200.1 (m, 1F, F^4).

3.4.2. Reaction of IF_7 with pentafluorophenyltrifluorosilane

A cold (−70 °C) solution of CH_3CN (12 mg, 0.29 mmol) in PFP (0.1 mL) and a cold (−40 °C) solution of $C_6F_5SiF_3$ (**8**) (34 mg, 0.13 mmol) in PFP (0.2 mL) were added in sequence to a cold (−70 °C) solution of IF_7 (0.10 mmol) in PFP (0.25 mL). The solution was stirred at −70 °C for 0.5 h and at −40 °C for 1 h. The ^{19}F NMR spectrum (−40 °C) showed signals of IF_7 and IF_5 (59:131), **9**, **10**, **11**, **6**, **7**, **12**, and SiF_4 (12:62:12:1:8:5:7). Stirring at 0 °C for 15 h resulted in the complete reduction of IF_7 to IF_5 accompanied by the corresponding changes in the molar ratio of products: **9**, **10**, **11**, **6**, **7**, **12**, and SiF_4 (0:36:36:1:9:3:9).

3.4.3. Reaction of IF_7 with $[Me_4N][C_6F_5SiF_4]$

A cold (−35 °C) solution of $C_6F_5SiF_3$ (40 mg, 0.157 mmol) in PFP (0.3 mL) was added to a cold (−70 °C) solution of $[Me_4N]F$ (18 mg, 0.193 mmol) in PFP (1.5 mL). A white suspension was formed which was stirred at −30 °C for 25 min before a cold (−35 °C) solution of IF_7 (0.158 mmol) in PFP (0.15 mL) was added in one portion. The suspension was stirred at −30 °C for 1 h and at 0 °C for 2 h before the colorless mother liquor was decanted. The precipitate (presumably, $[Me_4N]_2[SiF_6]$) was washed with PFB (1 mL). The ^{19}F NMR spectrum (0 °C) of the combined PFB solutions showed signals of **14**, **15**, **6**, **7**, **12**, and **13** (molar ratio 9:13:15:18:27:18) and unknown non-aromatic perfluoro compounds. Iodine heptafluoride was quantitatively converted into IF_5 (^{19}F NMR).

3.4.4. Reaction of IF_7 with pentafluorophenyldifluoroborane

A cold (−60 °C) solution of $C_6F_5BF_2$ (0.12 mmol) in PFP (0.25 mL) was added to a cold (−60 °C) stirred solution of IF_7 (0.15 mmol) in PFP (0.3 mL). The solution was stirred at −60 °C for 1 h. The ^{19}F NMR spectrum (−60 °C) contained signals of IF_5, BF_3, **6**, **7**, and broadened resonances of **17**, **18**, and **19** in the molar ratio 200:40:3:20:4:49:7 (C_4F_9Br as internal integral standard). Further stirring at 25 °C for 24 h led to the loss of BF_3 whereas the quantities of the other products were not changed. Now the fine structure of the ^{19}F resonances of perfluorocycloalkenyldifluoroboranes **17**, **18**, and **19** became available for analysis.

cyclo-1,3-C_6F_7-1-BF_2 (**17**). ^{19}F NMR (PFP): δ −74.3 (s, $\Delta\nu_{1/2}$ = 72 Hz, BF_2), −93.4 (d $^3J(F^2, F^3)$ = 16 Hz, t $^4J(F^2, F^6)$ = 16 Hz, 1F, F^2), −112.8 (m, d $^4J(F^6, F^2)$ = 16 Hz, 2F, F^6), −123.9 (m, 2F, F^5), −147.1 (t $^5J(F^3, F^6)$ = 5 Hz, d $^3J(F^3, F^2)$ = 16 Hz, t $^4J(F^3, F^5)$ = 19 Hz, 1F, F^3), −150.1 (m, t $^3J(F^4, F^5)$ = 17 Hz, 1F, F^4). ^{11}B NMR (PFP): δ 21 (s, $\Delta\nu_{1/2}$ = 76 Hz, BF_2).

cyclo-1-BF_2-1,4-C_6F_7 (**18**). ^{19}F NMR (PFP): δ −74.3 (s, $\Delta\nu_{1/2}$ = 72 Hz, 2F, BF_2), −98.2 (t $^5J(F^6, F^3)$ = 5 Hz, d $^4J(F^6, F^2)$ = 11 Hz, d $^4J(F^6, F^4)$ = 11 Hz, d $^3J(F^6, F^5)$ = 20 Hz, 2F, F^6), −102.4 (t $^4J(F^2, F^6)$ = 11 Hz, t $^3J(F^2, F^3)$ = 22 Hz, 1F, F^2), −112.3 (t $^5J(F^3, F^6)$ = 4 Hz, d $^3J(F^3, F^2)$ = 22 Hz, d $^4J(F^3, F^5)$ = 11 Hz, d $^3J(F^3, F^4)$ = 19 Hz, 2F, F^3), −150.9 (d $^5J(F^5, F^2)$ = 2 Hz, d $^3J(F^5, F^4)$ = 4 Hz, t $^4J(F^5, F^3)$ = 11 Hz, t $^3J(F^5, F^6)$ = 20 Hz, 1F, F^5), −158.1 (d $^4J(F^4, F^2)$ = 2 Hz, d $^3J(F^4, F^5)$ = 4 Hz, t $^4J(F^4, F^6)$ = 11 Hz, t $^3J(F^4, F^3)$ = 19 Hz, 1F, F^4). ^{11}B NMR (PFP): δ 21.1 (s, $\Delta\nu_{1/2}$ = 76 Hz, BF_2).

cyclo-1-BF_2-1-C_6F_9 (**19**). ^{19}F NMR (PFP), δ −74.3 (s, $\Delta\nu_{1/2}$ = 72 Hz, 2F, BF_2), −98.4 (m, 1F, F^2), −103.8 (m, 2F, F^6), −119.8 (m, d $^3J(F^3, F^2)$ = 22 Hz, 2F, F^3), −133.5 (m, 2F, F^4), −133.2 (m, 2F, F^5). ^{11}B NMR (PFP): δ 21.1 (s, $\Delta\nu_{1/2}$ = 76 Hz, BF_2).

3.4.5. Reaction of IF_7 with tetrafluorophenylen-1,4-bis(difluoroborane)

A cold (−65 °C) solution of 1,4-$C_6F_4(BF_2)_2$ (0.08 mmol) in PFP (1 mL) was added to a cold (−65 °C) stirred solution of IF_7 (0.08 mmol) in PFP (0.4 mL). The solution was stirred at −60 °C for 1 h. The ^{19}F NMR spectrum (−60 °C) contained signals of IF_5, **22**, and **23** in the molar ratio 100:30:60 (C_4F_9Br as internal integral standard). A second portion of IF_7 (0.08 mmol) in PFP (0.4 mL) was added at −60 °C. After stirring for 1 h at −60 °C and at −40 °C, the ^{19}F NMR spectrum (−40 °C) showed resonances of IF_5, **23**, **19**, and **7** in the molar ratio 240:30:7:13. No remarkable changes were observed in the ^{19}F NMR spectrum of the solution after 9 h at 25 °C, although in the ^{11}B NMR spectra now BF_3 (9.2 ppm) appeared. On long standing at 25 °C (≥4 days), **23** isomerized to **22** while the other products remained unchanged.

cyclo-1,3-C_6F_6-1,4-(BF_2) (**22**). ^{19}F NMR (PFP, −60 °C): δ −75.1 (s, $\Delta\nu_{1/2}$ = 330 Hz, 4F, BF_2), −96.3 (t $^4J(F^2, F^6)$ and $^4J(F^3, F^5)$ = 16 Hz, 2F, $F^{2,3}$), −113.8 (d $^4J(F^6, F^2)$ and $^4J(F^5, F^3)$ = 16 Hz, 4F, $F^{5,6}$). ^{11}B NMR (PFP, −60 °C): δ 20.4 (s, $\Delta\nu_{1/2}$ = 360 Hz, BF_2).

cyclo-1,4-C_6F_6-1,4-(BF_2) (**23**). ^{19}F NMR (PFP, −60 °C): δ −75.1 (s, $\Delta\nu_{1/2}$ = 330 Hz, 4F, BF_2), −98.1 (t $^4J(F^2, F^6)$ and $^4J(F^5, F^3)$ = 11 Hz, t $^3J(F^2, F^3)$ and $^3J(F^5, F^6)$ = 22 Hz, 2F, $F^{2,5}$), −99.0 (d $^3J(F^3, F^2)$ and $^3J(F^6, F^5)$ = 22 Hz, d $^4J(F^3, F^5)$ and $^4J(F^6, F^2)$ = 11 Hz, 4F, $F^{5,6}$). ^{11}B NMR (PFP, −60 °C): δ 20.4 (s, $\Delta\nu_{1/2}$ = 360 Hz, BF_2).

3.5. Attempts to fluorinate iodine in polyfluoroorganyliodine compounds

3.5.1. Reaction of pentafluorophenyliodine tetrafluoride with IF_7

A cold (−60 °C) solution of IF_7 (0.15 mmol) in PFP (0.3 mL) was added to a cold (−60 °C) stirred fine suspension of $C_6F_5IF_4$ (**24**) (54 mg, 0.145 mmol) in PFP (0.4 mL). The reaction mixture was stirred at −60 to −20 °C with periodic control of composition by ^{19}F NMR spectroscopy (PFB as internal integral standard). The molar ratio of IF_5:**20**:**14**:**15**:**24** was 60:22:27:0:192 (20% conversion, −60 °C, 1.5 h), 107:40:48:0:152 (36% conversion, −40 °C, 1 h), 177:63:78:4:90 (62% conversion, −40 °C, 3 h), and 270:88:115:14:16 (93% conversion, −40 to −30 °C, 12 h).

3.5.2. Reaction of iodopentafluorobenzene (excess) with IF_7

A cold (−50 °C) solution of IF_7 (0.10 mmol) in PFP (0.40 mL) was added to a cold (−45 °C) solution of C_6F_5I (48 mg, 0.163 mmol) in PFP (0.20 mL). Immediately a white precipitate was formed. The suspension was stirred at −40 °C for 40 min and at 0 °C for 1 h. The mother liquor was decanted at 0 °C and the residue was dissolved in cold (0 °C) MeCN (0.4 mL). The amount of $C_6F_5IF_2$ (0.08 mmol), IF_5 (0.06 mmol), and C_6F_5I (0.06 mmol) was determined from both solutions by ^{19}F NMR (C_6F_6 as quantitative integral standard).

3.5.3. Reaction of 2,2,2-trifluoroethyliodine tetrafluoride with IF_7

A cold (0 °C) solution of $CF_3CH_2IF_4$ (0.10 mmol) in PFB (0.12 mL) was added to a cold (−30 °C) solution of IF_7 (0.10 mmol) in PFP (0.30 mL). After stirring at 25 °C for 16 h the solution showed no reaction (^{19}F NMR).

3.5.4. Reaction of pentafluorophenyliodine tetrafluoride with $[O_2][SbF_6]$

Salt $[O_2][SbF_6]$ (148 mg, 0.55 mmol) was added to the cold (−65 °C) stirred suspension of $C_6F_5IF_4$ (99 mg, 0.26 mmol) in aHF (2 mL). The suspension was stirred at −30 °C (1 h) and at 0 °C (1 h). A probe of the mother liquor showed only ^{19}F NMR signals of $C_6F_5IF_4$ and aHF. The suspension was extracted with dichloromethane (1 mL) at 0 °C. The extract contained $C_6F_5IF_4$ (nearly quantitative recovery) (^{19}F NMR).

3.5.5. Reaction of 2,2,2-trifluoroethylliodine tetrafluoride with $[O_2][SbF_6]$ in basic HF

A cold (−20 °C) solution of $CF_3CH_2IF_4$ (0.24 mmol) and KF (0.48 mmol) in aHF (2 mL) was added to a cold (−65 °C) stirred suspension of $[O_2][SbF_6]$ (117 mg, 0.43 mmol) in aHF (3 mL). The suspension was warmed to 24 °C within 2 h and formed a colorless solution which was stirred for further 24 h. The quantity of $CF_3CH_2IF_4$ did not change (^{19}F NMR, 0 °C).

3.5.6. Reaction of 2,2,2-trifluoroethylliodine with $[O_2][SbF_6]$ in basic HF

A 11.7-mm i.d. PFA trap equipped with a magnetic stir bar was charged with $[O_2][SbF_6]$ (157 mg, 0.58 mmol) and cooled to 0 °C before aHF (3 mL) was added. After cooling the solution to −65 °C a cold (−55 °C) solution of KF (153 mg, 2.63 mmol) in aHF (0.6 mL) was added. A suspension was formed which was stirred at −65 °C for 40 min. CF_3CH_2I (24 mg, 0.11 mmol) was injected. The suspension was stirred at −65 °C (40 min), −40 °C (15 min), and −20 °C (20 min). When deposited in an ice bath the suspension transformed into a colorless solution. After 1 h a probe contained CF_3CH_2I and $CF_3CH_2IF_4$ (78:22) (^{19}F NMR, 0 °C).

3.5.7. Reaction of 2,2,2-trifluoroethylliodine tetrafluoride with $K_2[NiF_6]$ in basic HF

A cold (0 °C) solution of $CF_3CH_2IF_4$ (0.2 mmol) in aHF (0.3 mL) was added to a cold (0 °C) stirred deep-purple solution of $K_2[NiF_6]$ (80 mg, 0.31 mmol) and KF (18 mg, 0.31 mmol) in aHF (0.5 mL). Immediately a pale-brown precipitate was formed. After centrifugation at 0 °C, the colorless mother liquid was decanted. It contained $CF_3CH_2IF_4$, IF_5, CF_3CH_2F, and CF_3CHF_2 (100:262:31:23) (^{19}F NMR). The precipitate became greenish-yellow when residual HF was evaporated.

3.6. Fluorine addition to "non" polarized C=C double bonds in perfluoroolefins with IF_7

3.6.1. Reaction of perfluorohex-1-ene with IF_7

A cold (−65 °C) solution of $C_4F_9CF{=}CF_2$ (0.10 mmol) in PFP (0.17 mL) was added to a cold (−65 °C) solution of IF_7 (0.10 mmol) in PFP (0.30 mL). The solution was stirred at −60 °C for 2 h (no reaction, ^{19}F NMR). Further stirring at −30 °C for 2 h showed the quantitative formation of IF_5 and C_6F_{14} (1:1, ^{19}F NMR).

3.6.2. Reaction of perfluoro-4-methylpent-2-ene with IF_7

A cold (−30 °C) solution of $(CF_3)_2CFCF{=}CFCF_3$ (**31**) (*cis*:*trans* = 12:88) (0.10 mmol) in PFP (0.14 mL) was added to a cold (−25 °C) solution of IF_7 (0.10 mmol) in PFP (0.30 mL). The solution was stirred at −30 °C for 2 h (no reaction, ^{19}F NMR), at 24 °C for 1 h (6% conversion of **31**), 16 h (60% conversion of **31**), and 27 h (74% conversion of **31**). After overall 60 h of reaction the solution contained perfluoroisohexane and IF_5 besides traces of **31**, $(CF_3)_2CFCOF$ (34.2 (septet $^4J(F^1, CF_3) = 6$ Hz, d $^3J(F^1, F^2) = 22$ Hz, 1F, F^1), −73.5 (d $^3J(F^3, F^2) = 8$ Hz, d $^4J(CF_3, F^1) = 6$ Hz, 6F, CF_3), −180.0 (septet $^3J(F^2, CF_3) = 8$ Hz, d $^3J(F^2, F^1) = 22$ Hz, 1F, F^2) ppm (cf. [37])) CF_3COF (15.8 (q $^3J(F^1, F^2) = 6$ Hz, 1F, F^1), −74.0 (d $^3J(F^2, F^1) = 6$ Hz, 3F, F^2) ppm (cf. [38]), $(CF_3)_2CO$ (−86.0 (s) ppm (cf. [38]),) and C_2F_5COF (24.8 (t $^3J(F^1, F^2) = 9$ Hz, q $^4J(F^1, F^3) = 5$ Hz, 1F, F^1), −82.5 (d $^3J(F^3, F^1) = 5$ Hz, t $^3J(F^3, F^2) = 2$ Hz, 3F, F^3), −120.9 (q $^3J(F^2, F^3) = 2$ Hz, d $^3J(F^2, F^1) = 9$ Hz, 2F, F^2) (cf. [39])) (^{19}F NMR).

$(CF_3)_2CFC_3F_7$ (**33**). ^{19}F NMR (PFP, 0 °C): δ −71.1 (d 6 Hz, t 8.5 Hz, t 11 Hz, 6F, $2CF_3$), −79.8 (t 12 Hz, 3F, F^5), −114.4 (m, 2F, F^3), −124.1 (m, 2F, F^4), −185.1 (m, 1F, F^2). {lit. δ −73 ($2CF_3$), −82 ($1CF_3$), −115 (2F, F^3), −124 (2F, F^4), −185 (1F, F^2) [40]; −72.3 ($2CF_3$), −81 ($1CF_3$), −115 (2F, F^3), −125 (2F, F^4), −185.5 (1F, F^2) [41]}.

4. Conclusions

PFP and PFB are suitable solvents for IF_7. They withstand the oxidation property of IF_7 and allow to investigate the reactivity of IF_7 towards organoelement and organo compounds. Two promising routes to hitherto unknown R_FIF_6 were investigated, but without positive result concerning the goal. Instead, insight into the reactivity of IF_7 towards polyfluoroorganoelement compounds was obtained. The substitution of F by C_6F_5 which was successful in case of $HalF_n$ (Hal = Br, I; $n = 3, 5$) and XeF_n ($n = 2, 4$) comes in case of IF_7 to a preparative limitation: the rate of substitution decreases with increasing oxidation number (n) of iodine and parallel to n the oxidation power of $HalF_n$ increases. Principally, the C_6F_5 group offers relatively high nucleophilicity in combination with acceptable resistance to oxidizers. But this group can undergo fluorine addition to the C=C bonds under the action of IF_7. The alternative route to R_FIF_6 molecules, the fluorine addition to iodine in the corresponding precursors $C_6F_5IF_4$ and $CF_3CH_2IF_4$ did not lead to the target molecule R_FIF_6. $[O_2][SbF_6]$/HF is a no efficient fluoro-oxidizer for $C_6F_5IF_4$. IF_7/PFP attacks the C=C bonds of $C_6F_5IF_4$. $CF_3CH_2IF_4$ is inert to IF_7 in PFP/PFB and $[O_2][SbF_6]$ in aHF. Furthermore, $CF_3CH_2IF_4$ does not lead to the target molecule $CF_3CH_2IF_6$ with $K_2[NiF_6]$ under increased oxidizing conditions in "basic" aHF.

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