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Preparation of polyfluorinated cycloalk-1-enyl-, alk-1-enyl-, and alkyliodine tetrafluorides using XeF_2 in the presence of appropriate Lewis acids as fluorooxidant

Hermann Josef Frohn [a,*], Vadim V. Bardin [b]

[a] *Department of Chemistry, Inorganic Chemistry, University Duisburg-Essen, Lotharstr. 1, D-47048 Duisburg, Germany*
[b] *N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, SB RAS, Acad. Lavrentjev Ave. 9, 630090 Novosibirsk, Russia*

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Dedicated to Professor Herbert W. Roesky on the occasion of his 70th birthday.

Abstract

Previously unknown polyfluorocyclohexenyl, and acyclic perfluoroalkenyliodine tetrafluorides were prepared in high yields. Perfluorocyclohex-1-enyliodine tetrafluoride was obtained from pentafluoroiodobenzene using XeF_2–NbF_5 in aHF. The reaction of C_6F_5I with the weaker fluorooxidant XeF_2–BF_3 in 1,1,1,3,3-pentafluorobutane (PFB) yielded $C_6F_5IF_2$, perfluorocyclohexa-1,4-dienyliodine difluoride, $C_6F_5IF_4$, perfluorocyclohexa-1,4, and 1,3-dienyliodine tetrafluoride as intermediate products on parallel reaction routes. Both perfluoroalkenyl iodides, *cis*- and *trans*-$(CF_3)_2CFCF{=}CFI$, reacted with XeF_2–BF_3 in PFB to give the corresponding perfluoroalkenyliodine tetrafluorides, *cis*- and *trans*-$(CF_3)_2CFCF{=}CFIF_4$. Even perfluoroalkyl iodides can be fluorinated by this reagent as was demonstrated by the preparation of $C_6F_{13}IF_4$ from $C_6F_{13}I$. Generally, the $CF{=}CIF_n$ fragment ($n = 0$, 2, or 4) in cyclic or acyclic perfluoroalkenyliodine compounds R_FIF_n did not undergo a transformation to the corresponding perfluoroalkyliodine compound. Furthermore, no perfluoroorganoiodine hexafluorides were detected in reactions with the fluorooxidant XeF_2–aHF or BF_3 or NbF_5.

Keywords: Xenon difluoride; Fluorine addition; Organoiodine(V) tetrafluorides

1. Introduction

Organic derivatives of iodine(III) and iodine(V) are well-established compounds with a variety of applications. In general, the organic chemistry of iodine(V) is much less developed than the chemistry of iodine(III). The synthesis and some properties of alkyl- and aryliodine(V) fluorides were described [1], whereas alkenyliodine(V) compounds are not known till recently.

Three principal routes to alkenyliodine(V) derivatives can be discussed: (a) the introduction of an alkenyl group into a suitable I(V) compound, (b) the oxidation of alkenyl iodide or an alkenyliodine(III) parent compound to the desired alkenyliodine(V) compound, and (c) the transformation of a suitable organoiodine(V) compound into the related alkenyliodine(V) compound.

A promising route to polyfluoroalkenyliodine tetrafluorides is based on the oxidative addition of fluorine to polyfluorinated aryliodine(V) derivatives. In 1974, Winfield and co-workers obtained $C_6F_5IF_4$ by the reaction of C_6F_5I with chlorine trifluoride in perfluorohexane when they warmed the reaction mixture from −78 °C to room temperature [2]. Under similar conditions, the reaction of either $C_6F_5IF_4$ or C_6F_5I with ClF_3 in large excess gave $C_6ClF_8IF_4$ and $C_6Cl_2F_7IF_4$ (presumably, polyfluorinated cyclohexenyliodine tetrafluorides), the constitution of which was not studied [2]. On the other hand, heating of molten $C_6F_5IF_2$ with xenon difluoride at 60–65 °C for 3 h led to the quantitative formation of $C_6F_5IF_4$ without fluorine addition

* Corresponding author. Tel.: +49 203 379 3310; fax: +49 203 379 2231.
E-mail address: frohn@uni-duisburg.de (H.J. Frohn).

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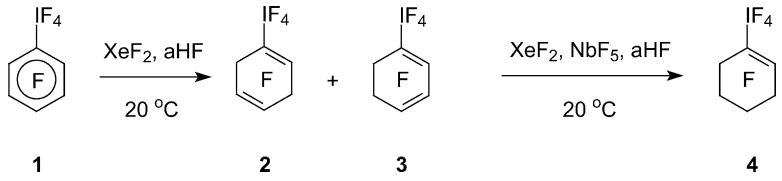


Scheme 1.

to the pentafluorophenyl group [3]. In the presence of Lewis acids the fluorinating ability of xenon difluoride is raised strongly caused by either the polarisation of the xenon–fluorine bond in case of a relatively weak fluoride anion acceptor or the complete ionisation to [FXe][Y] under the action of a strong fluoride anion acceptor. Previously, we have successfully employed xenon difluoride in the presence of Lewis acids (aHF, BF_3, SbF_5) to convert polyfluoroarenes bearing either electron donating ($SiMe_3$, $SiMe_2F$, $SiMe_2C_6F_5$, $GeEt_3$) or electron withdrawing (F, Cl, Br, NO_2, CN, CF_3, SiF_3, GeF_3, Xe^+) substituents into the corresponding polyfluorocycloalkenyl derivatives [4–9]. In our present investigation we use this kind of oxidative fluorinating reaction for the preparation of polyfluoroorganoiodine(V) tetrafluorides [10].

2. Results and discussion

2.1. Preparation of polyfluorocycloalk-1-enyliodine tetrafluorides

When a suspension of $C_6F_5IF_4$ (**1**) in aHF was treated with two equivalents of XeF_2 at −5 to 20 °C, xenon evolved and perfluorinated cyclohexa-1,4-dienyliodine tetrafluoride (**2**), cyclohexa-1,3-dienyliodine tetrafluoride (**3**) and unreacted xenon difluoride were detected in the mother liquor. No further fluorine addition to dienes **2** and **3** occurred at 20 °C within the next 3 h. However, after addition of niobium pentafluoride (stronger fluoride anion acceptor than HF) to the suspension the fast formation of perfluorocyclohex-1-enyliodine tetrafluoride (**4**) resulted in 89% yield (Scheme 1).

Scheme 1 demonstrates the higher fluorinating ability of [FXe][NbF_6] generated in situ from XeF_2 and NbF_5 compared to that of the polarised complex [FXe···F···HF] and offers the opportunity for the aimed formation of **4** directly from iodopentafluorobenzene (**5**). Indeed, treatment of **5** with xenon difluoride in the presence of a catalytic amount (ca. 10 mol.%) of NbF_5 in aHF gave **4** in 72% yield (Scheme 2).

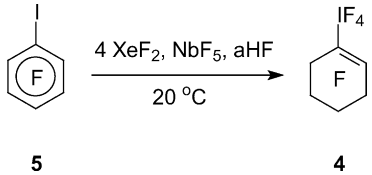
The conversion of iodoarene **5** to cyclohexenyliodine tetrafluoride **4** (Scheme 2) can primarily proceed as an oxidative fluorination of the iodine atom ($C_6F_5I \rightarrow C_6F_5IF_2 \rightarrow C_6F_5IF_4$) with the subsequent fluorine addition to the C=C bonds of **1**, **2**, and **3**, respectively ($C_6F_5IF_4 \rightarrow C_6F_7IF_4 \rightarrow C_6F_9IF_4$) (Scheme 1). Alternatively, the fluorination of the pentafluorophenyl group can run parallel to the addition of fluorine to iodine. To get more insight into the fluorinating process, we studied the reaction of xenon difluoride with pentafluorophenyliodine difluoride (**6**) and with iodopentafluorobenzene (**5**) in the presence of the weak Lewis acid boron trifluoride in the inert solvent 1,1,1,3,3-pentafluorobutane (PFB) [11].

Xenon difluoride (one equivalent) did not react with a solution of **6** in PFB at 0 °C within 5 min, but a slow bubbling of BF_3 at 0 °C caused the immediate formation of a white precipitate and vigorous evolution of gas. After stirring at 20 °C for 2 h the mother liquor contained perfluorocyclohexa-1,4-dienyliodine difluoride (**7**), $C_6F_5IF_4$ (**1**), and dienes $C_6F_7IF_4$ (**2**, **3**) beside unchanged pentafluorophenyliodine difluoride (**6**). The subsequent addition of XeF_2 (four equivalents) caused dissolution of the precipitate and finally perfluorinated cyclohexadienyliodine tetrafluoride **2** and cyclohexenyliodine tetrafluoride **4** (70:30) were obtained in quantitative yield (Scheme 3).

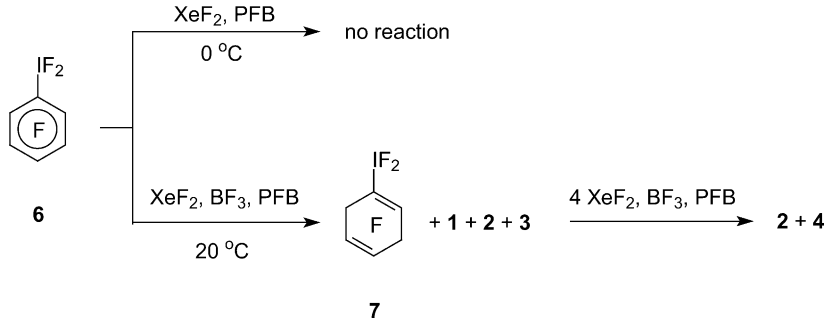
The reaction of **5** with XeF_2 (four equivalents) in PFB in the presence of boron trifluoride at ≤20 °C gave a solution of perfluorocyclohexa-1,4-dienyliodine difluoride (**7**), $C_6F_5IF_4$ (**1**), and dienes $C_6F_7IF_4$ (**2**, **3**) beside a trace of **4**, however aryl iodide **5** and aryliodine difluoride **6** were not detected. The further reaction with XeF_2 (additional one equivalent) under BF_3-catalysis resulted in the conversion of **7** and **1** into cyclic alkenyliodine tetrafluorides **2**, **3**, and **4** in 90% overall yield (Scheme 4).

These results are in agreement with the following reaction route (Scheme 5) from iodopentafluorobenzene (**5**) to perfluorocyclohexenyliodine tetrafluoride (**4**) using xenon difluoride catalysed by Lewis acids (aHF, BF_3, and NbF_5).

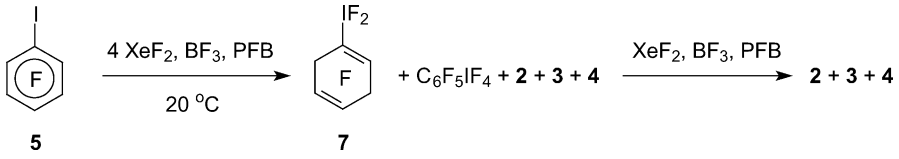
In the first step iodopentafluorobenzene (**5**) is rapidly converted into $C_6F_5IF_2$ (**6**) which accidentally corresponds with the quantitative formation of **6** from **5** and XeF_2 in CH_2Cl_2 at 20 °C [3]. Pentafluorophenyliodine difluoride reacts with XeF_2 as fluorooxidant on two channels: (a) by the fluorine addition to the pentafluorophenyl group and (b) to the IF_2 group. The subsequent Lewis acid-catalysed addition



Scheme 2.



Scheme 3.



Scheme 4.

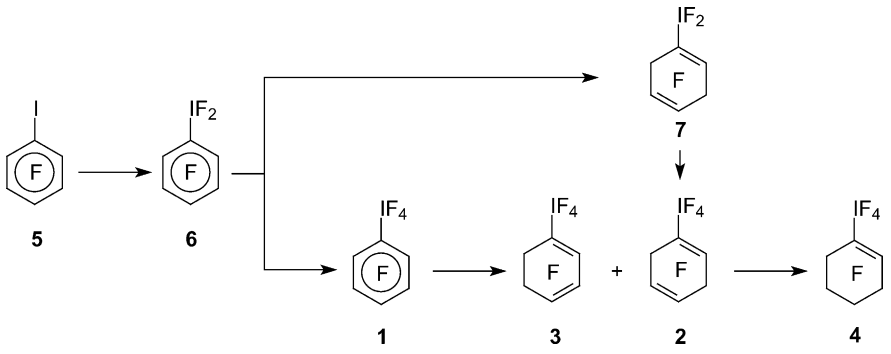
of two fluorine atoms to diene $C_6F_7IF_2$ (**7**) leads to cyclohexadienyliodine tetrafluoride **2** (diene **7** did not react with XeF_2 in CH_2Cl_2 without Lewis acid-catalyst at 50 °C [12]). **2** and its isomer **3** are also products of the parallel addition of fluorine to $C_6F_5IF_4$. Finally, both cyclohexadienyliodine tetrafluorides **2** and **3** undergo oxidative addition of fluorine across the FC=CF fragment to yield cyclohexenyliodine tetrafluoride **4**. The formation of organoiodine(VII) compounds as well as perfluorocyclohexyliodine tetrafluoride did not occur.

Our earlier investigations of reactions of tetrafluorobenzenes C_6HF_4R (R=H, F, Br, CF_3, NO_2 [7], $SiMe_3$ [8], $Xe^+[AsF_6]^-$ [5]) with XeF_2 and $BF_3{\cdot}OEt_2$ in CH_2Cl_2 or with XeF_2 in aHF showed that the addition of fluorine to the polyfluorinated aromatic group was accompanied by the partial substitution of the hydrogen atom in position 2 or 3 to substituent R. The hydrogen atom located in position 4 was not replaced by fluorine in any case. This circumstance was explained within the framework of the one electron transfer mechanism induced by the strong fluorooxidant $[FXe]^+$ or a structurally related polarised species generated from xenon difluoride [7]. 2,3,4,5-Tetrafluorophenyliodine tetrafluoride (**8**) was a substrate of particular interest because of the strong inductive effect of the IF_4 group and its weak resonance effect ($\sigma_I = 0.98$, $\sigma_R = 0.17$ [13]).

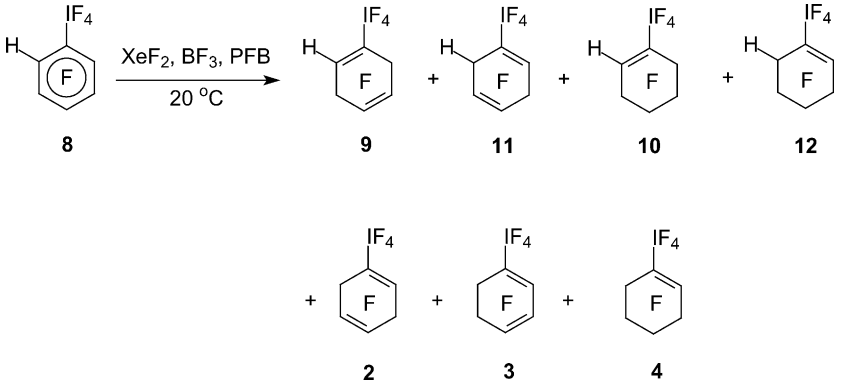
Compound **8** did not react with XeF_2 in PFB but in the presence of boron trifluoride polyfluorinated cycloalkenyliodine tetrafluorides were formed. The main products were 2-H-hexafluorocyclohexa-1,4-dienyliodine tetrafluoride (**9**), 2-H-octafluorocyclohex-1-enyliodine tetrafluoride (**10**), 6-H-hexafluorocyclohexa-1,4-dienyliodine tetrafluoride (**11**) and 6-H-octafluorocyclohex-1-enyliodine tetrafluoride (**12**). In a parallel route, a significant amount of perfluorinated cycloalkenyliodine tetrafluorides **2**, **3**, and **4** were formed (Scheme 6).

The reaction of 1-iodo-2,3,5,6-tetrafluorobenzene (**13**) with XeF_2 (excess) and BF_3 in PFB resulted in hydrogen-containing cycloalkenyliodine tetrafluorides **14**, **15**, and **16**. Here no substitution of hydrogen by fluorine occurred (Scheme 7).

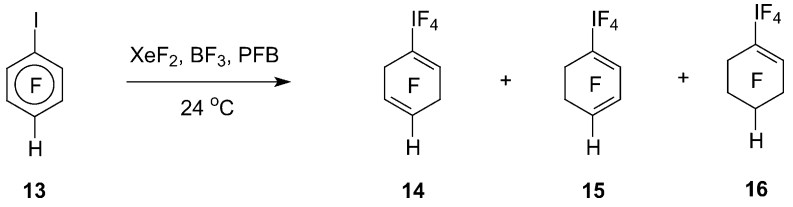
Both examples well complete the previous view of the fluorine addition to polyfluoroaromatic groups [7].



Scheme 5.



Scheme 6.



Scheme 7.

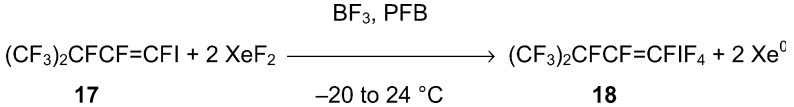
2.2. Preparation of perfluoroalk-1-enyliodine tetrafluoride and perfluoroalkyliodine tetrafluoride by fluorination with XeF_2

The remarkable peculiarity of all examples discussed before is the absence of poly- and perfluorocyclohexyliodine di- and tetrafluorides among the reaction products. This implies that (a) the oxidative addition of fluorine to iodine in aryl iodides proceeds much faster than the fluorine addition across the FC=CF and FC=CI double bonds in the polyfluoroaromatic group and (b) that the FC=CIF_n fragments ($n = 2$, 4) resist to the oxidative fluorination under the conditions of reaction described here. Hence, these circumstances provide the opportunity to prepare acyclic perfluoroalk-1-en-1-yliodine tetrafluorides from the corresponding perfluorinated alkenyl iodides under similar reaction conditions. To extend the fluorination with XeF_2–Lewis acid on acyclic compounds, we examined the reaction of 1-iodoperfluoro-3-methylbut-1-enes (*cis*: *trans* = 12:88) (**17**) with XeF_2 in PFB in the presence of boron trifluoride.

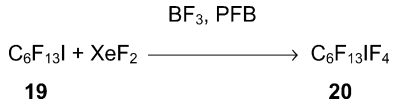
The treatment of **17** in PFB with xenon difluoride (two equivalents) with a slow bubbling of BF_3 resulted in perfluoro-3-methylbut-1-enyliodine tetrafluorides **18** (*cis*: *trans* = 1:9) in high yield. Noteworthy, that at the end of the reaction neither the formation of 1-iodoperfluoro-3-methylbutane nor perfluoro-3-methylbutyliodine di- and tetrafluoride was detected (Scheme 8).

The formation of perfluorohexyliodine tetrafluoride (**20**) from perfluorohexyl iodide (**19**) and xenon difluoride in the presence of BF_3 shows that this method of fluorination can even be extended to the class of perfluoroalkyliodine tetrafluorides (Scheme 9). In summary, the last examples complete the general character of this route to polyfluorinated organoiodine tetrafluorides.

Finally, it should be emphasised that perfluoroorganoiodine tetrafluorides R_FIF_4 resist to the strong protic acid aHF, to acidified aHF (aHF–NbF_5), and to the Lewis acid boron trifluoride at 20–22 °C for some hours. The only effect of interaction of R_FIF_4 with these acids was the broadening of the IF_4 signal in the ^{19}F NMR spectra and the disappearance of the spin–spin coupling of the IF_4 nuclei with CF_x ones of the perfluoroorgano group in R_FIF_4 (for example, see Section 4). This phenomenon indicates a fast exchange of fluoride between R_FIF_4 and the Lewis acid (fluoride anion acceptor) without complete ionisation to organoiodonium(V) trifluoride cations. The degree of broadening increases in the series $C_6F_{13}IF_4 < (CF_3)_2CFCF{=}CFIF_4 <$ *cyclo*-$C_6F_9IF_4$ which points out the diminishing of the electron-withdrawing effect of the perfluoroorgano group



Scheme 8.



Scheme 9.

which is mainly influenced by the number of electron-wthdrawing fluorine atoms at the carbon atom C(1).

3. Conclusions

The fluorooxidant XeF_2–BF_3 in PFB allows the addition of fluorine in perfluoroorganyl iodide and perfluoroorganoiodine difluoride and finally ends with perfluoroorganoiodine tetrafluorides. In case of iodopentafluorobenzene as starting compound addition of fluorine to the pentafluorophenyl group proceeds forming cyclohexadienyliodine and cyclohexenyliodine tetrafluorides beside fluorine addition to iodine. No perfluorocyclohexyliodine tetrafluoride was obtained, even in the presence of the stronger Lewis acid NbF_5 in aHF.

It seems to be a general feature that molecules with the fragment CF=CIF_4 do not undergo fluorine addition across this C=C double bond under the action of XeF_2 and BF_3 or NbF_5. Furthermore this fluorooxidant does not allow fluorine addition to the IF_4 group and formation of the hitherto unknown organoiodine hexafluorides.

Fluorination of perfluoroalkenyl and polyfluoroaryl iodides, polyfluoroaryliodine di- and tetrafluorides with XeF_2 and Lewis acid (aHF, BF_3, NbF_5) results in previously unknown organoiodine compounds, alk-1-enyliodine tetrafluorides and cycloalk-1-enyliodine tetrafluorides.

The Lewis acid-catalysed fluorine addition to $C_6F_5IF_4$ and $C_6HF_4IF_4$ using xenon difluoride occurs in the same way as the corresponding addition reactions to pentafluoro- (C_6F_5R) and tetrafluorobenzene derivatives (C_6HF_4R) [6–8]. This means the same or a closely related mechanism of reaction.

The formation of organoiodine(VII) as well as perfluorocyclohexyliodine tetrafluoride was not detected even under the action of the strong fluorinating agent XeF_2–NbF_5–aHF.

Reactions of perfluoroalkyl iodides R_FI with XeF_2 in PFB under catalysis of BF_3 are a simple and convenient laboratory route to perfluoroalkyliodine tetrafluorides R_FIF_4.

4. Experimental details

NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (^1H at 300.13 MHz and ^{19}F at 282.40 MHz) at 24 °C. The chemical shifts are referenced to TMS (^1H) and CCl_3F (^{19}F) [with C_6F_6 as a secondary reference (−162.9 ppm)]. The composition of the reaction mixtures and the yields of products were determined by ^{19}F NMR spectroscopy using the internal quantitative standards 1,1,2-trichlorotrifluoroethane or C_6F_6. 1-X-nonafluorocyclohexenes [14] and 1-X-heptafluorocyclohexadienes [15] were identified by their ^{19}F NMR spectra.

$C_6F_5IF_2$ was prepared by a modified low temperature fluorination of C_6F_5I in CCl_3F [16]. $C_6F_5IF_4$ was obtained by reaction of $Bi(C_6F_5)_3$ and IF_5 in MeCN [17]. $(CF_3)_2CFCF{=}CFI$ [18] was kindly given by Dr. Cherstkov (INEOS RAN, Russia). Dichloromethane (Baker), acetonitrile (Riedel-deHaën) were purified and dried by standard procedures. Iodopentafluorobenzene, 2,3,4,5-tetrafluoroiodobenzene, 2,3,5,6-tetrafluoroiodobenzene (Bristol Organics), 1-iodoperfluorohexane (Clariant), 1,1,1,3,3-pentafluorobutane (Solvay), and boron trifluoride (Messer Griesheim) were used as supplied. NbF_5 was distilled in FEP (block copolymer of tetrafluoroethylene and hexafluoropropylene) equipment before use. Anhydrous HF was stored over CoF_3.

All manipulations were performed in FEP equipment under an atmosphere of dry argon.

4.1. Preparation of polyfluorocycloalk-1-enyliodine tetrafluorides

4.1.1. Starting from pentafluorophenyliodine compounds

*4.1.1.1. Fluorination of C_6F_5I (**5**) with XeF_2 and BF_3 in PFB.* A solution of **5** (92 mg, 0.31 mmol) in PFB (2 ml) was cooled to −13 °C and XeF_2 (214 mg, 1.27 mmol) was added in one portion. Boron trifluoride was slowly bubbled through the stirred reaction mixture, which was finally allowed to warm to 20 °C. After 25 min a probe of the colourless solution showed the presence of **7**, **1**, **2**, **3**, and **4** (molar ratio 9:11:60:17:3) (^{19}F NMR). A second portion of XeF_2 (47 mg, total amount 1.54 mmol) was added and the solution was stirred for further 30 min with bubbling of BF_3. The ^{19}F NMR spectrum showed resonances of **2**, **3**, and **4** (molar ratio 76:18:6) beside **7** and IF_5 (traces). The solution was evaporated to dryness under reduced pressure to give a white solid (128 mg) that consisted of **2** (0.21 mmol), **3** (0.03 mmol) and **4** (0.04 mmol) (molar ratio **2**:**3**:**4** = 76:10:14).

*4.1.1.2. Fluorination of C_6F_5I (**5**) with XeF_2 and NbF_5 in aHF.* Xenon difluoride (430 mg, 2.54 mmol) and NbF_5 (38 mg, 0.20 mmol) were dissolved in aHF (2 ml) at 0 °C and C_6F_5I (**5**) (140 mg, 0.47 mmol) was added in portions. After 5 min the solution was warmed to 18–20 °C (bath) and stirred for 1.5 h. To destroy the excess of XeF_2, C_6F_6 (ca. 0.05 ml) was added at 10 °C. This solution was stirred at 15–17 °C for 10–15 min. The products were extracted with anhydrous dichloromethane (3 ml) at −20 °C. The extract was treated with NaF, the suspension was centrifuged and the solvent was removed in vacuum to give **4** (152 mg, 72%).

*4.1.1.3. Fluorination of $C_6F_5IF_2$ (**6**) with XeF_2 and BF_3 in PFB.* A solution of **6** (111 mg, 0.33 mmol) in PFB (2 ml)

was cooled to 0 °C and XeF_2 (62 mg, 0.36 mmol) was added in one portion. No reaction was observed within 5 min. Then BF_3 was slowly bubbled through for 2 h at 20 °C. Precipitation and gas evolution occurred. A second portion of XeF_2 (226 mg, total amount 1.70 mmol) was added and stirring was continued for 1 h at 20 °C with bubbling of BF_3. The solid part of the suspension dissolved. After addition of C_6F_6 (excess) to decompose residual XeF_2 the solution was concentrated under reduced pressure. The solution contained **2**, **4** (70:30) (quantitative yield) and IF_5 (trace).

Heptafluorocyclohexa-1,4-dienyliodine tetrafluoride (**2**). ^{19}F NMR (CH_2Cl_2): δ −5.9 (t $^4J(IF_4, F^6)$ = 18 Hz, d $^4J(IF_4, F^2)$ = 28 Hz, 4F, IF_4), −95.9 (m, 2F, $F^{6,6}$), −96.9 (m, 1F, F^2), −110.1 (t $^5J(F^3, F^6)$ = 3 Hz, d $^4J(F^3, F^5)$ = 10 Hz, d $^3J(F^3, F^4)$ = 20 Hz, d $^3J(F^3, F^2)$ = 24 Hz, 2F, $F^{3,3}$), −148.8 (m, 1F, F^5), −158.2 (d $^3J(F^4, F^5)$ = 5 Hz, t $^3J(F^4, F^3)$ = 21 Hz, t $^4J(F^4, F^6)$ = 10 Hz, 1F, F^4).

Heptafluorocyclohexa-1,4-dienyliodine tetrafluoride (**2**). ^{19}F NMR (PFB, saturated with BF_3): δ −95.9 (t $^5J(F^6, F^3)$ = 4 Hz, d $^4J(F^6, F^2)$ = 10 Hz, d $^4J(F^6, F^4)$ = 10 Hz, d $^3J(F^6, F^5)$ = 21 Hz, 2F, $F^{6,6}$), −97.6 (d $^5J(F^2, F^5)$ = 1 Hz, d $^4J(F^2, F^4)$ = 3 Hz, t $^4J(F^2, F^6)$ = 10 Hz, t $^3J(F^2, F^3)$ = 22 Hz, 1F, F^2), −110.8 (t $^5J(F^3, F^6)$ = 4 Hz, d $^4J(F^3, F^5)$ = 11 Hz, d $^3J(F^3, F^4)$ = 19 Hz, d $^3J(F^3, F^2)$ = 22 Hz, 2F, $F^{3,3}$), −150.6 (d $^5J(F^5, F^2)$ = 1 Hz, d $^3J(F^5, F^4)$ = 4 Hz, t $^4J(F^5, F^3)$ = 11 Hz, t $^3J(F^5, F^6)$ = 21 Hz, 1F, F^5), −160.1 (d $^4J(F^4, F^2)$ = 3 Hz, d $^3J(F^4, F^5)$ = 4 Hz, t $^4J(F^4, F^6)$ = 10 Hz, 1F, F^4).

Heptafluorocyclohexa-1,3-dienyliodine tetrafluoride (**3**). ^{19}F NMR (CH_2Cl_2): δ −8.6 (t $^4J(IF_4, F^6)$ = 14 Hz, d $^4J(IF_4, F^2)$ = 23 Hz, 4F, IF_4), −89.8 (m, 1F, F^2), −113.2 (m, 2F, $F^{6,6}$), −126.3 (m, d $^4J(F^5, F^3)$ = 15 Hz, d $^3J(F^5, F^4)$ = 19 Hz, 2F, $F^{5,5}$), −144.2 (t $^3J(F^4, F^5)$ = 18 Hz, d $^4J(F^4, F^2)$ = 18 Hz, 1F, F^4), −148.3 (d $^3J(F^3, F^2)$ = 9 Hz, t $^4J(F^3, F^5)$ = 15 Hz, 1F, F^3).

Heptafluorocyclohexa-1,3-dienyliodine tetrafluoride (**3**). ^{19}F NMR (PFB, saturated with BF_3): δ −90.8 (d $^3J(F^2, F^3)$ = 6 Hz, d $^4J(F^2, F^4)$ = 17 Hz, t $^3J(F^2, F^6)$ = 17 Hz, 1F, F^2), −113.1 (m, d $^4J(F^6, F^4)$ = 4 Hz, d $^4J(F^6, F^2)$ = 17 Hz, 2F, $F^{6,6}$), −126.9 (m, d $^4J(F^5, F^3)$ = 14 Hz, d $^3J(F^5, F^4)$ = 18 Hz, 2F, $F^{5,5}$), −146.8 (t $^4J(F^4, F^6)$ = 4 Hz, t $^3J(F^4, F^5)$ = 18 Hz, d $^4J(F^4, F^2)$ = 17 Hz, 1F, F^4), −150.3 (d $^3J(F^3, F^2)$ = 6 Hz, t $^4J(F^3, F^5)$ = 14 Hz, 1F, F^3).

Nonafluorocyclohex-1-enyliodine tetrafluoride (**4**). ^{19}F NMR (CH_2Cl_2): δ −5.1 (t $^4J(IF_4, F^6)$ = 17 Hz, d $^4J(IF_4, F^2)$ = 28 Hz, 4F, IF_4), −93.7 (m, 1F, F^2), −104.0 (m, 2F, $F^{6,6}$), −117.1 (m, d $^3J(F^3, F^2)$ = 25 Hz, 2F, $F^{3,3}$), −133.1 (m, 2F, $F^{5,5}$), −133.6 (m, 2F, $F^{4,4}$).

Nonafluorocyclohex-1-enyliodine tetrafluoride (**4**). ^{19}F NMR (PFB, saturated with BF_3): δ −94.4 (m, 1F, F^2), −103.8 (m, 2F, $F^{6,6}$), −117.7 (m, d $^3J(F^3, F^2)$ = 24 Hz, 2F, $F^{3,3}$), −133.5 (m, 2F, $F^{5,5}$), −134.0 (m, 2F, $F^{4,4}$).

*4.1.1.4. Fluorination of $C_6F_5IF_4$ (**1**) with XeF_2 in aHF.* A suspension of **1** (199 mg, 0.53 mmol) in aHF (0.3 ml) was cooled to −5 °C and XeF_2 (182 mg, 1.07 mmol) was added in portions. After each addition, the reaction mixture was warmed to 20 °C until xenon evolution came to an end. Finally the suspension was stirred at 20 °C for 20 min. The ^{19}F NMR spectrum contained resonances of **2**, **3**, and XeF_2 (molar ratio 2:1:1.3) beside aHF and a trace of IF_5. No changes occurred when the suspension was kept at 20 °C for 3 h. The suspension was cooled to −5 °C, NbF_5 (70 mg, 0.37 mmol) was added and the reaction mixture was stirred at 20 °C for 15 min. Hydrogen fluoride was removed in vacuum, the residue was extracted with dichloromethane and cyclohexene **4** (white solid) (211 mg, 89%) was obtained after removal of the solvent in vacuum (^{19}F NMR).

4.1.2. Starting from tetrafluorophenyliodine compounds

*4.1.2.1. Synthesis of 2,3,4,5-tetrafluorophenyliodine tetrafluoride (**8**).* **8** was prepared from 2,3,4,5-tetrafluoroiodobenzene and XeF_2 via 2,3,4,5-tetrafluorophenyliodine difluoride according to the procedure described for the preparation of pentafluorophenyliodine tetrafluoride [3].

2,3,4,5-Tetrafluorophenyliodine difluoride. 2,3,4,5-Tetrafluoroiodobenzene (580 mg, 2.10 mmol) and XeF_2 (395 mg, 2.31 mmol) were heated at 40–45 °C (bath) for 1 h under an atmosphere of dry argon. After cooling to 20 °C the product 2,3,4,5-$C_6HF_4IF_2$ (white solid) was obtained (642 mg, 97%).

^{19}F NMR (CH_2Cl_2): δ −120.9 (d $^3J(F^2, F^3)$ = 20 Hz, d $^4J(F^2, F^4)$ = 4 Hz, d $^5J(F^2, F^5)$ = 8 Hz, d $^4J(F^2, H^6)$ = 5 Hz, 1F, F^2), −134.9 (d $^4J(F^5, F^3)$ = 3 Hz, d $^3J(F^5, F^4)$ = 20 Hz, d $^3J(F^5, H^6)$ = 13 Hz, d $^5J(F^5, F^2)$ = 8 Hz, 1F, F^5), −146.0 (d $^3J(F^4, F^5)$ = 20 Hz, d $^3J(F^4, F^3)$ = 19 Hz, d $^4J(F^4, H^6)$ = 8 Hz, d $^4J(F^4, F^2)$ = 4 Hz, 1F, F^4), −150.0 (d $^3J(F^3, F^2)$ = 20 Hz, d $^3J(F^3, F^4)$ = 19 Hz, d $^5J(F^3, H^6)$ = 4 Hz, d $^4J(F^3, F^5)$ = 3 Hz, 1F, F^3), −161.1 (s, 2F, IF_2); ^1H NMR (CH_2Cl_2): δ 7.94 (m, 1H, H^6).

2,3,4,5-Tetrafluorophenyliodine tetrafluoride (**8**). 2,3,4,5-Tetrafluorophenyliodine difluoride (573 mg, 1.82 mmol) and XeF_2 (450 mg, 2.66 mmol) were heated at 90–110 °C (bath) for 12 h under an atmosphere of dry argon. The melt was cooled to 20 °C and treated in vacuum for 4 h yielding 2,3,4,5-$C_6HF_4IF_4$ (white solid) (602 mg, 94%).

^{19}F NMR (PFB): δ −14.1 (d $^4J(IF_4, F^2)$ = 21 Hz, 4F, IF_4), −129.8 (quint $^4J(F^2, IF_4)$ = 21 Hz, d $^3J(F^2, F^3)$ = 19 Hz, d $^5J(F^2, F^5)$ = 10 Hz, d $^4J(F^2, F^4)$ = 11 Hz, d $^4J(F^2, H^6)$ = 5 Hz, 1F, F^2), −136.2 (d $^5J(F^5, F^2)$ = 10 Hz, d $^4J(F^5, F^3)$ = 4 Hz, d $^3J(F^5, F^4)$ = 19 Hz, d $^3J(F^5, H^6)$ = 10 Hz, 1F, F^5), −145.9 (d $^3J(F^4, F^3)$ = 19 Hz, d $^3J(F^4, F^5)$ = 19 Hz, d $^4J(F^4, F^2)$ = 11 Hz, d $^4J(F^4, H^6)$ = 8 Hz, 1F, F^4), −152.0 (m, d $^3J(F^3, F^2)$ = 19 Hz, d $^3J(F^3, F^4)$ = 19 Hz, 1F, F^3); ^1H NMR (CH_2Cl_2): δ 7.91 (m, 1H, H^6).

*4.1.2.2. Fluorination of 2,3,4,5-$C_6HF_4IF_4$ (**8**) with XeF_2 and BF_3 in PFB.* XeF_2 (100 mg, 0.59 mmol) was added to a stirred suspension of **8** (204 mg, 0.58 mmol) in PFB (2 ml) at 20 °C. The reaction mixture was stirred for further 3 min but no gas evolution could be observed. The suspension was cooled to 0 °C (bath) and a slight flow of BF_3 was bubbled through and caused dissolution of **8**. After 5 min a second

portion of XeF_2 (250 mg, total amount 2.07 mmol) was added. The solution was stirred at 20 °C for 1 h with a slow bubbling of BF_3 and then treated with C_6F_6 (ca. 0.05 ml) to reduce the surplus of XeF_2 and after 15 min with dry NaF to remove BF_3. The mother liquor was separated after centrifugation. The ^{19}F NMR spectrum showed the formation of **2** (0.10 mmol), **3** (0.02 mmol), **4** (0.02 mmol), **9** (0.25 mmol), **10** (0.06 mmol), **11** (0.04 mmol), **12** (0.05 mmol), and IF_5 (0.05 mmol) beside 1,4-C_6F_8 (from C_6F_6) and unreacted C_6F_6 and XeF_2 (0.33 mmol). When this solution was maintained at 20 °C for further 48 h, no changes in the ^{19}F NMR spectrum were observed.

2-H-Hexafluorocyclohexa-1,4-dienyliodine tetrafluoride (**9**). ^{19}F NMR (PFB): δ −12.9 (t $^4J(IF_4, F^6)$ = 15 Hz, 4F, IF_4), −101.1 (m, 2F, $F^{6,6}$), −103.0 (t $^5J(F^3, F^6)$ = 4 Hz, d $^3J(F^3, H^2)$ = 5 Hz, d $^4J(F^3, F^5)$ = 11 Hz, d $^3J(F^3, F^4)$ = 20 Hz, 2F, $F^{3,3}$), −153.0 (d $^3J(F^4, F^5)$ = 3 Hz, t $^4J(F^4, F^6)$ = 11 Hz, t $^3J(F^4, F^3)$ = 20 Hz, 1F, F^4), −157.1 (d $^3J(F^5, F^4)$ = 3 Hz, t $^4J(F^5, F^3)$ = 11 Hz, t $^3J(F^5, F^6)$ = 20 Hz, d $^5J(F^5, H^2)$ = 6 Hz, 1F, F^5); ^1H NMR (PFB): δ 7.59 (m, 1H, H^2).

2-H-Octafluorocyclohex-1-enyliodine tetrafluoride (**10**). ^{19}F NMR (PFB): δ −11.5 (t $^4J(IF_4, F^6)$ = 15 Hz, 4F, IF_4), −107.3 (m, 2F, $F^{6,6}$), −108.9 (m, 2F, $F^{3,3}$), −133.8 (m, 2F) and −134.6 (m, 2F) ($F^{4,4}$ and $F^{5,5}$); ^1H NMR (PFB): δ 7.58 (m, 1H, H^2).

6-H-Hexafluorocyclohexa-1,4-dienyliodine tetrafluoride (**11**). ^{19}F NMR (PFB): δ −15.4 (d $^4J(IF_4, F^6)$ = 14 Hz, d $^4J(IF_4, F^2)$ = 24 Hz, 4F, IF_4), −99.7 (m, 1F, F^2), −105.9 (m, d $^2J(F^{3A}, F^{3B})$ = 305 Hz, 1F, F^{3A}), −111.3 (m, d $^2J(F^{3B}, F^{3A})$ = 305 Hz, 1F, F^{3B}), −136.3 (m, d $^3J(F^5, F^6)$ = 32 Hz, 1F, F^5), −160.0 (m, 1F, F^4), −173.0 (m, 1F, F^6); ^1H NMR (PFB): δ 6.34 (m, d $^2J(H^6, F^6)$ = 47 Hz, 1H, H^6).

6-H-Octafluorocyclohex-1-enyliodine tetrafluoride (**12**). ^{19}F NMR (PFB): δ −16.5 (d $^4J(IF_4, F^6)$ = 6 Hz, d $^4J(IF_4, F^2)$ = 23 Hz, 4F, IF_4), −97.1 (m, 1F, F^2), −110.4 (m, d $^3J(F^{3A}, F^2)$ = 28 Hz, d $^2J(F^{3A}, F^{3B})$ = 295 Hz, 1F, F^{3A}), −125.8 (m, d $^2J(F^{3B}, F^{3A})$ = 295 Hz, 1F, F^{3B}), −122.9 (m, d $^2J(F^{4A}, F^{4B})$ = 286 Hz, 1F, F^{4A}), −131.0 (m, d $^2J(F^{4B}, F^{4A})$ = 286 Hz, 1F, F^{4B}), −123.1 (m, d $^2J(F^{5A}, F^{5B})$ = 278 Hz, 1F, F^{5A}), −140.8 (m, d $^2J(F^{5B}, F^{5A})$ = 278 Hz, 1F, F^{5B}), −178.2 (m, 1F, F^6) (the assignment of F^4 and F^5 is tentative); ^1H NMR (PFB): δ 6.07 (m, d $^2J(H^6, F^6)$ = 46 Hz, 1H, H^6).

*4.1.2.3. Fluorination of 2,3,5,6-C_6HF_4I (**13**) with XeF_2 and BF_3 in PFB.* XeF_2 (370 mg, 2.18 mmol) was added to the stirred solution of **13** (122 mg, 0.44 mmol) in PFB (2 ml) at −15 °C and a slight flow of BF_3 was passed through the solution. After 15 min the bath was removed and the colourless solution was stirred at 24 °C for 1 h with a slow bubbling of BF_3. Hexafluorobenzene (ca. 0.05 ml) was added and the solution was stirred for further 30 min. The solution was concentrated under reduced pressure to ca. 1.5 ml volume and treated with dry NaF. The ^{19}F NMR spectrum showed resonances of **14**, **15**, and **16** (68:11:21) (total yield 0.38 mmol) beside IF_5 (trace), 1,4-C_6F_8 (from C_6F_6) and XeF_2 (0.34 mmol). Continued supply of BF_3 into the solution for 1 h at 24 °C led to the disappearance of XeF_2 and the partial conversion of **15** into **16** (molar ratio **14**:**15**:**16** = 67:6:27) (^{19}F NMR).

4-H-Hexafluorocyclohexa-1,4-dienyliodine tetrafluoride (**14**). ^{19}F NMR (PFB): δ −6.7 (t $^4J(IF_4, F^6)$ = 18 Hz, d $^4J(IF_4, F^2)$ = 24 Hz, 4F, IF_4), −94.7 (m, 1F, F^2), −97.3 (m, 2F, $F^{6,6}$), −98.8 (t $^5J(F^3, F^6)$ = 3 Hz, d $^3J(F^3, H^4)$ = 5 Hz, d $^4J(F^3, F^5)$ = 12 Hz, d $^3J(F^3, F^2)$ = 23 Hz, 2F, $F^{3,3}$), −120.9 (d $^5J(F^5, F^2)$ = 2 Hz, d $^3J(F^5, H^4)$ = 10 Hz, t $^4J(F^5, F^3)$ = 12 Hz, t $^3J(F^5, F^6)$ = 21 Hz, 1F, F^5); ^1H NMR (PFB): δ 6.00 (m, 1H, H^4).

4-H-Hexafluorocyclohexa-1,4-dienyliodine tetrafluoride (**14**). ^{19}F NMR (PFB saturated with BF_3): δ −94.7 (d $^5J(F^2, F^5)$ = 2 Hz, d $^4J(F^2, H^4)$ = 6 Hz, t $^4J(F^2, F^6)$ = 11 Hz, t $^3J(F^2, F^3)$ = 23 Hz, 1F, F^2), −97.3 (d $^4J(F^6, H^4)$ = 2 Hz, t $^5J(F^6, F^3)$ = 3 Hz, d $^4J(F^6, F^2)$ = 11 Hz, d $^3J(F^6, F^5)$ = 21 Hz, 2F, $F^{6,6}$), −98.8 (t $^5J(F^3, F^6)$ = 3 Hz, d $^3J(F^3, H^4)$ = 5 Hz, d $^4J(F^3, F^5)$ = 12 Hz, d $^3J(F^3, F^2)$ = 23 Hz, 2F, $F^{3,3}$), −120.9 (d $^5J(F^5, F^2)$ = 2 Hz, d $^3J(F^5, H^4)$ = 10 Hz, t $^4J(F^5, F^3)$ = 12 Hz, t $^3J(F^5, F^6)$ = 21 Hz, 1F, F^5). The broad resonance ($\tau_{1/2} \approx 400$ Hz) of the IF_4 group was located at −6.6 ppm.

4-H-Hexafluorocyclohexa-1,3-dienyliodine tetrafluoride (**15**). ^{19}F NMR (PFB): δ −9.0 (t $^4J(IF_4, F^6)$ = 14 Hz, d $^4J(IF_4, F^2)$ = 23 Hz, 4F, IF_4), −92.0 (m, 1F, F^2), −113.5 (m, 2F, $F^{6,6}$), −117.0 (d $^3J(F^5, H^4)$ = 5 Hz, d $^5J(F^5, F^2)$ = 5 Hz, d $^4J(F^5, F^3)$ = 16 Hz, 2F, $F^{5,5}$), −119.9 (d $^3J(F^3, F^2)$ = 8 Hz, t $^5J(F^3, F^6)$ = 1 Hz, d $^3J(F^3, H^4)$ = 7 Hz, t $^4J(F^3, F^5)$ = 16 Hz, 1F, F^3); ^1H NMR (PFB): δ 6.00 (m, 1H, H^4).

4-H-Hexafluorocyclohexa-1,3-dienyliodine tetrafluoride (**15**). ^{19}F NMR (PFB saturated with BF_3): δ −92.0 (d $^3J(F^2, F^3)$ = 8 Hz, d $^4J(F^2, H^4)$ = 7 Hz, t $^4J(F^2, F^6)$ = 17 Hz, 1F, F^2), −113.5 (m, d $^4J(F^6, F^2)$ = 17 Hz, 2F, $F^{6,6}$), −117.0 (d $^3J(F^5, H^4)$ = 5 Hz, d $^5J(F^5, F^2)$ = 5 Hz, d $^4J(F^5, F^3)$ = 16 Hz, 2F, $F^{5,5}$), −119.9 (d $^3J(F^3, F^2)$ = 8 Hz, t $^5J(F^3, F^6)$ = 1 Hz, d $^3J(F^3, H^4)$ = 7 Hz, t $^4J(F^3, F^5)$ = 16 Hz, 1F, F^3). The broad resonance ($\tau_{1/2} \approx 400$ Hz) of the IF_4 group was located at −6.6 ppm.

4-H-Octafluorocyclohex-1-enyliodine tetrafluoride (**16**). ^{19}F NMR (PFB): δ −5.8 (d $^4J(IF_4, F^{6A})$ = 15 Hz, d $^4J(IF_4, F^{6B})$ = 18 Hz, d $^4J(IF_4, F^2)$ = 27 Hz, 4F, IF_4), −94.7 (m, 1F, F^2), −99.4 (m, d $^2J(F^{6A}, F^{6B})$ = 287 Hz, 1F, F^{6A}), −107.9 (m, d $^2J(F^{6B}, F^{6A})$ = 287 Hz, 1F, F^{6B}), −106.3 (m, d $^2J(F^{3A}, F^{3B})$ = 298 Hz, 1F, F^{3A}), −115.3 (m, d $^2J(F^{3B}, F^{3A})$ = 298 Hz, 1F, F^{3B}), −127.8 (m, d $^2J(F^{5A}, F^{5B})$ = 266 Hz, 1F, F^{5A}), −130.2 (m, d $^2J(F^{5B}, F^{5A})$ = 266 Hz, 1F, F^{5B}), −222.3 (m, d $^2J(F^4, H^4)$ = 45 Hz, 1F, F^4); ^1H NMR (PFB): δ 5.17 (m, d $^2J(H^4, F^4)$ = 45 Hz, 1H, H^4).

4-H-Octafluorocyclohex-1-enyliodine tetrafluoride (**16**). ^{19}F NMR (PFB saturated with BF_3): δ −94.7 (m, 1F, F^2), −99.4 (m, d $^2J(F^{6A}, F^{6B})$ = 287 Hz, 1F, F^{6A}), −107.9 (m, d $^2J(F^{6B}, F^{6A})$ = 287 Hz, 1F, F^{6B}), −106.3 (m, d $^2J(F^{3A}, F^{3B})$ = 298 Hz, 1F, F^{3A}), −115.3 (m, d $^2J(F^{3B}, F^{3A})$ = 298 Hz, 1F, F^{3B}), −127.8 (m, d $^2J(F^{5A}, F^{5B})$ = 266 Hz, 1F, F^{5A}), −130.2 (m, d $^2J(F^{5B}, F^{5A})$ 266 Hz, 1F, F^{5B}), −222.3 (m, d $^2J(F^4, H^4)$ = 45 Hz, 1F, F^4). The broad resonance ($\tau_{1/2} \approx 400$ Hz) of the IF_4 group was located at −6.6 ppm.

4.2. Preparation of perfluoroalk-1-enyliodine and perfluoroalkyliodine tetrafluoride

4.2.1. Fluorination of $(CF_3)_2CFCF{=}CFI$ (17) with XeF_2 and BF_3 in PFB

XeF_2 (497 mg, 2.94 mmol) was added to a stirred solution of **17** (495 mg, 1.38 mmol) (*cis*:*trans* = 12:88) in PFB (3 ml) at 20 °C. After cooling to −20 °C (bath) a slight flow of BF_3 was bubbled through and immediately a white suspension was formed. After 3 min the suspension was allowed to warm to 25 °C. Dissolution of the solid proceeded. The slow bubbling of BF_3 was continued for 1 h with stirring. The solution was treated with C_6F_6 (ca. 0.02 ml) and after 5 min all volatile materials were removed in vacuum at 25 °C to give 500 mg (83%) of $(CF_3)_2CFCF{=}CFIF_4$ (**18**) (*cis*:*trans* = 1:9).

trans-Perfluoro-3-methylbut-1-enyliodine tetrafluoride (*trans*-**18**). ^{19}F NMR (CH_2Cl_2): δ −19.7 (d $^4J(IF_4, F^2)$ = 18 Hz, 4F, IF_4), −75.5 (d $^5J(CF_3, F^1)$ = 4 Hz, d $^4J(CF_3, F^2)$ = 8 Hz, d $^3J(CF_3, F^3)$ = 8 Hz, 6F, CF_3), −129.7 (m, d $^4J(F^1, F^3)$ = 50 Hz, d $^3J(F^1, F^2)$ = 135 Hz, 1F, F^1), −145.0 (m, d $^3J(F^2, F^1)$ = 135 Hz, 1F, F^2), −187.3 (sept $^3J(F^3, CF_3)$ = 8 Hz, d $^3J(F^3, F^2)$ = 11 Hz, d $^4J(F^3, F^1)$ = 50 Hz, 1F, F^3).

trans-Perfluoro-3-methylbut-1-enyliodine tetrafluoride (*trans*-**18**). ^{19}F NMR (PFB saturated with BF_3): δ −19.7 (br, 4F, IF_4), −75.6 (d $^5J(CF_3, F^1)$ = 4 Hz, d $^4J(CF_3, F^2)$ = 8 Hz, d $^3J(CF_3, F^3)$ = 8 Hz, 6F, CF_3), −129.8 (sept $^5J(F^1, CF_3)$ = 4 Hz, d $^4J(F^1, F^3)$ = 50 Hz, d $^3J(F^1, F^2)$ = 135 Hz, 1F, F^1), −145.1 (m, d $^3J(F^2, F^1)$ = 135 Hz, 1F, F^2), −187.5 (sept $^3J(F^3, CF_3)$ = 8 Hz, d $^3J(F^3, F^2)$ = 11 Hz, d $^4J(F^3, F^1)$ = 50 Hz, 1F, F^3).

cis-Perfluoro-3-methylbut-1-enyliodine tetrafluoride (*cis*-**18**). ^{19}F NMR (CH_2Cl_2): δ −12.3 (d $^4J(IF_4, F^2)$ = 41 Hz, 4F, IF_4), −74.6 (d $^3J(CF_3, F^3)$ = 9 Hz, d $^4J(CF_3, F^2)$ = 9 Hz, 6F, CF_3), −109.3 (d $^3J(F^1, F^2)$ = 36 Hz, 1F, F^1), −134.9 (m, 1F, F^2), −184.3 (m, 1F, F^3).

cis-Perfluoro-3-methylbut-1-enyliodine tetrafluoride (*cis*-**18**). ^{19}F NMR (PFB saturated with BF_3): δ −12.4 (br, 4F, IF_4), −74.7 (d $^3J(CF_3, F^3)$ = 7 Hz, d $^4J(CF_3, F^2)$ = 11 Hz, 6F, CF_3), −109.3 (d $^3J(F^1, F^2)$ = 36 Hz, 1F, F^1), −135.0 (sept $^4J(F^2, CF_3)$ = 11 Hz, d $^3J(F^2, F^1)$ = 36 Hz, 1F, F^2), −184.5 (m, 1F, F^3).

4.2.2. Fluorination of $C_6F_{13}I$ (19) with XeF_2 and BF_3 in PFB

Xenon difluoride (204 mg, 1.20 mmol) was added to a solution of **19** (223 mg, 0.50 mmol) in PFB (2 ml) and the suspension was stirred for 10 min at 25 °C. No reaction occurred. The suspension was cooled to −5 °C and BF_3 was bubbled through with stirring. Immediately white slurry was formed. After warming to 25 °C the solid dissolved and the colourless solution was stirred for 1 h with bubbling of BF_3. To destroy the excess of XeF_2, hexafluorobenzene (70 mg, 0.37 mmol) was added. All volatile materials were evaporated in vacuum to give viscous oil. The ^{19}F NMR spectrum of its solution in PFB showed the formation of **20** in quantitative yield.

Perfluorohexyliodine tetrafluoride (**20**). ^{19}F NMR (PFB): δ −27.7 (apparent pentet 4F, IF_4), −81.4 (t $^3J(F^6, F^5)$ = 2 Hz, t $^4J(F^6, F^4)$ = 10 Hz, 3F, $F^{6,6,6}$), −82.0 (m, 2F, $F^{1,1}$), −119.5 (m, 2F, $F^{2,2}$), −121.2 (m, 2F) and −122.4 (m, 2F) ($F^{3,3}$ and $F^{4,4}$), −126.2 (m, 2F, $F^{5,5}$). In the presence of BF_3 (24 °C) the resonance of the IF_4 group at −27.7 ppm became a broad singlet ($\tau_{1/2}$ = 78 Hz) whereas the position and multiplicity of all other resonances did not change.

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References

[1] (a) P.J. Stang, V.V. Zhdankin, Chem. Rev. 96 (1996) 1123–1178;
(b) A. Varvoglis, The Organic Chemistry of Polycoordinated Iodine, VCH Publishers, New York, 1992;
(c) A. Varvoglis, Hypervalent Iodine in Organic Synthesis, Academic Press, London, 1997.
[2] J.A. Berry, G. Oates, J.M. Winfield, J. Chem. Soc. Dalton Trans. (1974) 509–511.
[3] I.I. Maletina, V.V. Orda, N.N. Aleinikov, B.L. Korsunskii, L.M. Yagupolskii, J. Org. Chem. USSR 12 (1976) 1364 (Eng. Transl.).
[4] H.-J. Frohn, V.V. Bardin, J. Chem. Soc. Chem. Commun. (1993) 1072–1074.
[5] H.-J. Frohn, V.V. Bardin, Z. Naturforsch. 53B (1998) 562–564.
[6] V.V. Bardin, H.-J. Frohn, J. Fluorine Chem. 60 (1993) 141–151.
[7] V.V. Bardin, L.N. Shchegoleva, H.-J. Frohn, J. Fluorine Chem. 77 (1996) 153–159.
[8] V.V. Bardin, H.-J. Frohn, J. Fluorine Chem. 90 (1998) 93–96.
[9] V.V. Bardin, G.G. Furin, G.G. Yakobson, J. Org. Chem. USSR 18 (1982) 525–530 (Eng. Transl.).
[10] Preliminary communication: V.V. Bardin, H.-J. Frohn, P. Barthen, in: 12th Eur. Symp. on Fluorine Chemistry, Berlin (Germany), 29 August–2 September, 1998, PII-21.
[11] The use of PFB in preference to widely used dichloromethane for reactions of organic compounds with xenon difluoride in the presence of Lewis acids was discussed in Ref. [19].
[12] H.-J. Frohn, R. Nielinger, J. Fluorine Chem. 77 (1996) 143–146.
[13] C. Hansch, A. Leo, R.W. Taft, Chem. Rev. 91 (1991) 165–195.
[14] S.F. Campbell, A.G. Hudson, E.F. Mooney, A.E. Pedler, R. Stephens, K.N. Wood, Spectrochim. Acta 23A (1967) 2119–2125.
[15] V.V. Bardin, J. Fluorine Chem. 89 (1998) 195–211.
[16] F. Bailly, P. Barthen, W. Breuer, H.-J. Frohn, M. Giesen, J. Helber, G. Henkel, A. Priwitzer, Z. Anorg. Allg. Chem. 626 (2000) 1406–1413.
[17] H.-J. Frohn, S. Görg, G. Henkel, M. Läge, Z. Anorg. Allg. Chem. 621 (1995) 1251–1256.
[18] V.F. Cherstkov, M.V. Galakhov, S.R. Sterlin, L.S. German, I.L. Knunyants, Izv. AN SSSR. Ser. Khim. (1986) 119–122;
V.F. Cherstkov, M.V. Galakhov, S.R. Sterlin, L.S. German, I.L. Knunyants, Chem. Abstr. 106 (1986) 17830.
[19] H.-J. Frohn, N.Yu. Adonin, V.V. Bardin, Z. Anorg. Allg. Chem. 629 (2003) 2499–2508.