Reaction of perfluorinated alkyl-, alkenyl-, and cycloalkenyltetrafluoro--λ^5-iodanes R_FIF_4 with halide anions in non-aqueous solutions

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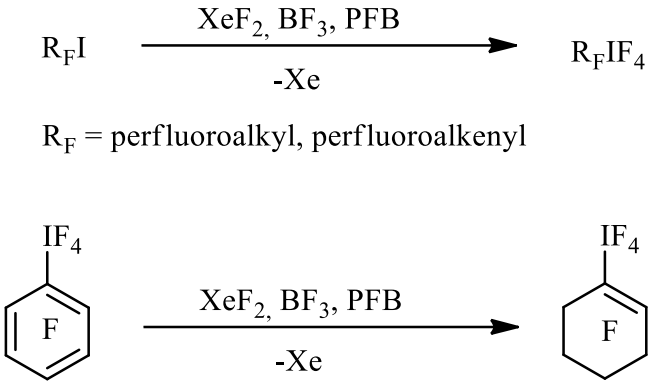
Abstract: *Perfluoroorganic derivatives of iodine(V) R_FIF_4 (R_F = C_6F_{13}, $(CF_3)_2CFCF{=}CF$, cyclo-C_6F_9) react with halide anions X^- (X = Cl, Br, I) in CH_2Cl_2 and/or in $CF_3CH_2CF_2CH_3$ (PFB) to give mainly iodides R_FI. In addition, the corresponding chlorides, bromides and R_F were formed. The relative contribution of processes depended on the constitution of perfluoroorganyl moiety. The influence of fluoride anions on the reaction route was studied too. Reaction of $[Me_4N]F$ with perfluorocyclohexen-1-yltetrafluoro-λ^5-iodane led to salt $[Me_4N][C_6F_{10}IF_4]$ while isomer $[Me_4N][1\text{-cyclo-}C_6F_9IF_5]$ was not detected.*

Key words: *perfluoroorganyltetrafluoro-λ^5-iodanes, reduction, perfluorocarbanions, NMR ^{19}F spectroscopy.*

Chemistry of organoiodine(III) is well studied and achievements in this field are presented in monographs and reviews. Properties of organic derivatives of iodine(V) are significantly less studied [1-7]. The same picture is observed in series of their poly- and perfluorinated analogues [8, 9].

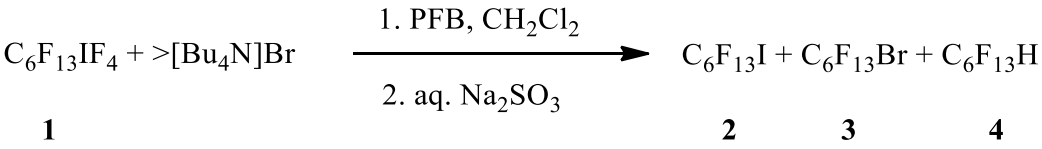
In 2005 we published the simple and convenient method of preparation of perfluorinated alkyl-, alkenyl- and cycloalkenyltetrafluoro-λ^5-iodanes R_FIF_4 by the oxidative fluorination of the corresponding iodides or aryltetrafluoro-λ^5-iodanes with xenon difluoride in the presence of BF_3 [10] (scheme 1).



Scheme 1

Chemical properties of these compounds were not investigated. Herein results of interaction of perfluorinated alkyl-, alkenyl- and cycloalkenyltetrafluoro-λ^5-iodanes R_FIF_4 with tetraalkylammonium fluoride, chloride, bromide and iodide in dichloromethane and/or PFB are presented.

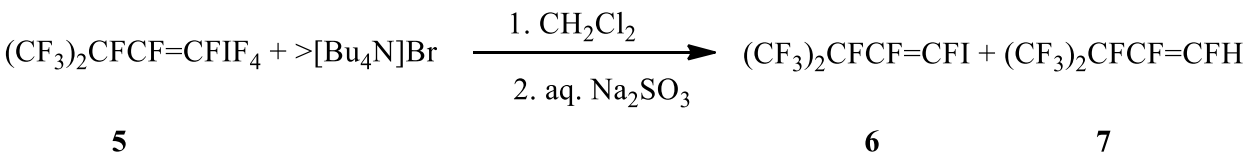
An addition of $C_6F_{13}IF_4$ (**1**) in PFB into solution of $[Bu_4N]Br$ (in excess) in dichloromethane followed hydrolysis gave a mixture of 1-iodoperfluorohexane (**2**), 1-bromoperfluorohexane (**3**) and 1-H-perfluorohexane (**4**) (molar ratio 5:1:1) in total quantitative yield (scheme 2).



Scheme 2

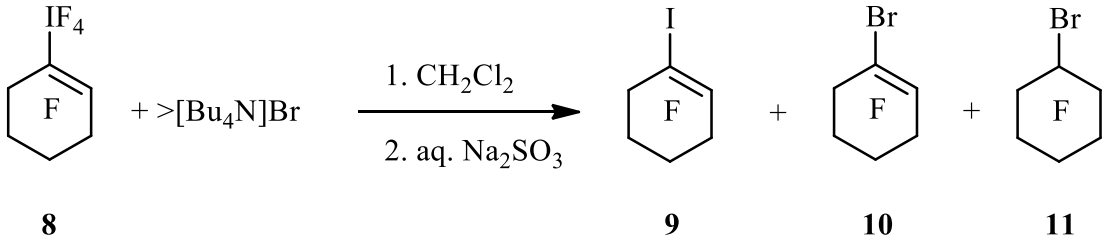
(Here and below an excess of reagent is marked by ">".)

Reaction of perfluoro-3-methylbuten-1-yltetrafluoro-λ^5-iodane (**5**) (*cis* : *trans* = 1 : 9) with $[Bu_4N]Br$ in CH_2Cl_2 led to 1-iodoperfluoro-3-methylbuten-1 (**6**) and a few trans-1-H-perfluoro-3-methylbuten-1 (**7**). The ratio *cis*-**6** : *trans*-**6** is the same as in started iodanes **5** (scheme 3).



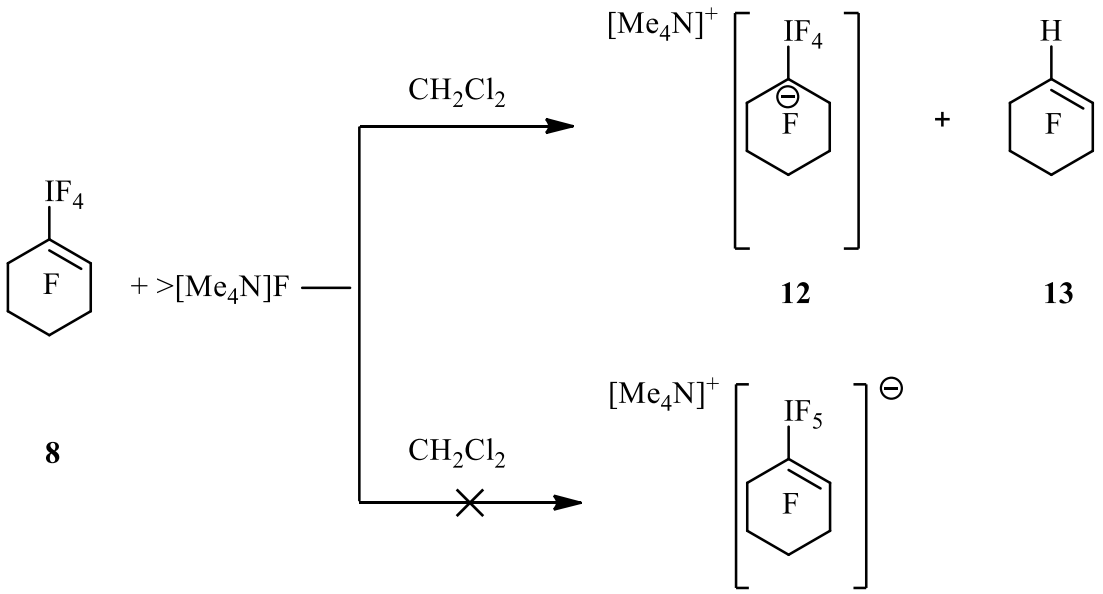
Scheme 3

Under the action of $[Bu_4N]Br$ perfluorocyclohexen-1-yltetrafluoro-λ^5-iodane (**8**) underwent to 1-iodoperfluorocyclohexene (**9**), 1-bromoperfluorocyclohexene (**10**), and bromoperfluorocyclohexane (**11**) (molar ratio 3 : 4 : 3) (scheme 4).



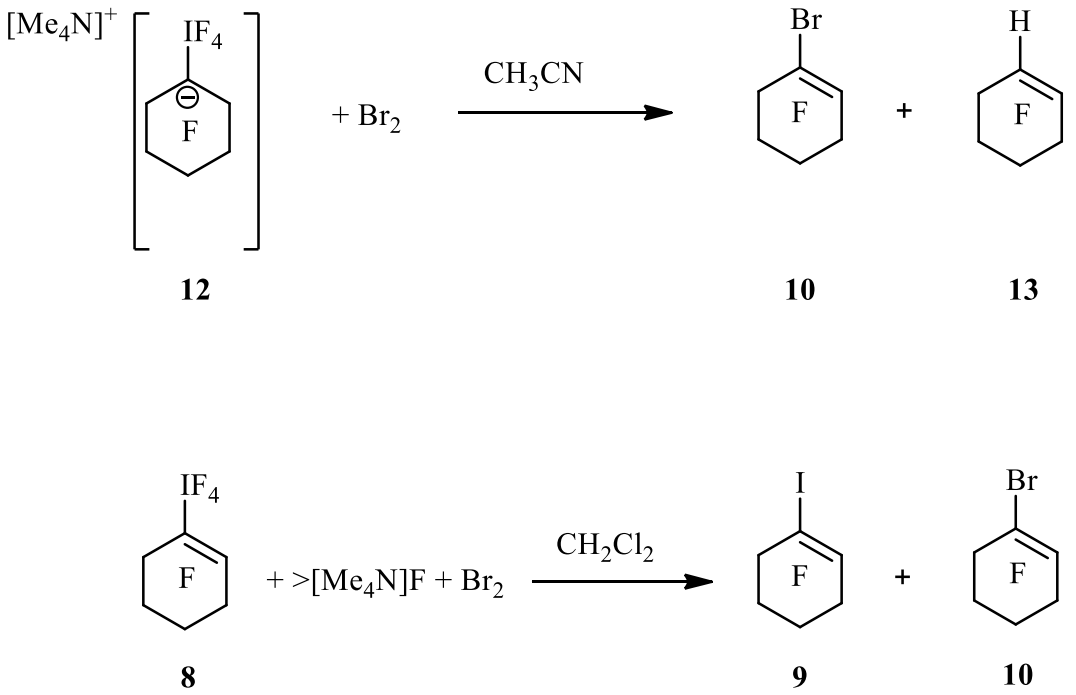
Scheme 4

These results show the processes of replacement of iodine atom by bromine and hydrogen atom that proceeded parallel to the reduction of λ^5-iodanes to iodides. Since during the reaction of fluoride anions are formed, we performed a reaction of λ^5-iodanes with the $[Me_4N]F$ as a "naked" fluoride donor. The action of $[Me_4N]F$ on $C_6F_{13}IF_4$ in EtCN gave $C_6F_{13}I$ (major) and $C_6F_{13}H$ (trace). Except they an admixture of unrecognized perfluorohexane derivative, $C_6F_{13}R$, was found (^{19}F NMR). Probably, the reducing agent here is propionitrile. The interaction of iodane **5** with $[Me_4N]F$ in MeCN yielded alkene **7** (trace) and substance which is insoluble either in MeCN and DMF (presumably, oligomer). An addition of $[Me_4N]F$ to a solution of **8** in CH_2Cl_2 at –40 °C and sequent warming to 22 °C led to suspension. The liquid phase contained a few 1-H-perfluorocyclohexene (**13**) but signals of iodane **8** and perfluorocyclohexenes **9** and **10** were not observed (^{19}F NMR). Precipitate was separated, washed with dichloromethane, dried in vacuum and dissolved in anhydrous MeCN. The ^{19}F NMR spectrum displayed resonances of cyclohexene **13**, IF_5, $[IF_6]^-$ and salt **12**. Signals of isomer $[cyclo\text{-}C_6F_9IF_5]^-$ that contained hexacoordinated iodine atom were not detected (scheme 5). Up to date, complex $[pip][C_6H_5IF_5]$ produced from hexamethylpiperidinium fluoride, [pip]F, and $C_6H_5IF_4$ is the only known representative of this family. It was characterized by ^{19}F NMR spectroscopy and X-ray data, but chemical properties were not described [12].



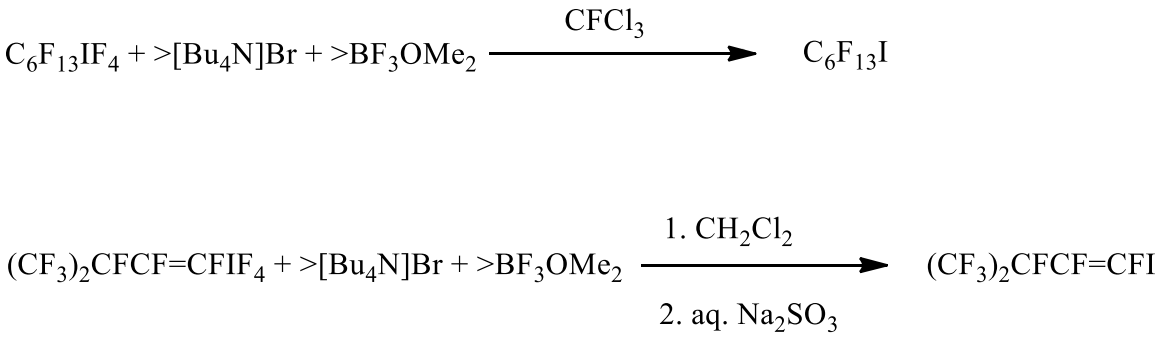
Scheme 5

Spectrum ^{19}F NMR of **12** displayed signals of IF_4 group at –13.4 (tt, $^4J(F_4I, F^{2,2})$ = 20 Hz, $^4J(F_4I, F^{6,6})$ = 20 Hz, 4F, IF_4) and cyclohexyl moiety at –89.3 (m, 4F, $F^{2,2,6,6}$), –128.9 (m, 4F, $F^{3,3,5,5}$) and –130.8 (m, 2F, $F^{4,4}$) ppm. These values are very close so perfluoro-1-ethyl-cyclohexan-1-ide [–79.5 (CF_3), –101.7 (CF_2), –87.0 (4F, $F^{2,2,6,6}$), –129.0 (4F, $F^{3,3,5,5}$) and –133.0 (2F, $F^{4,4}$) ppm], that was generated by an addition of fluoride anion to perfluoro-1-ethylcyclohexene [11]. At 22 °C salt **12** in MeCN converted slowly to cyclohexene **13** and IF_5 forming white precipitate. Within 18 h the ratio **12** : **13** was 1 : 1. After treatment of suspension with bromine cyclohexene **10** and additional amount of cyclohexene **13** were obtained (**10** : **13** = 1 : 2). It is interesting that the action of $[Me_4N]F$ and bromine on **8** in CH_2Cl_2 resulted in cyclohexenes **9** and **10** (1 : 9) (scheme 6).



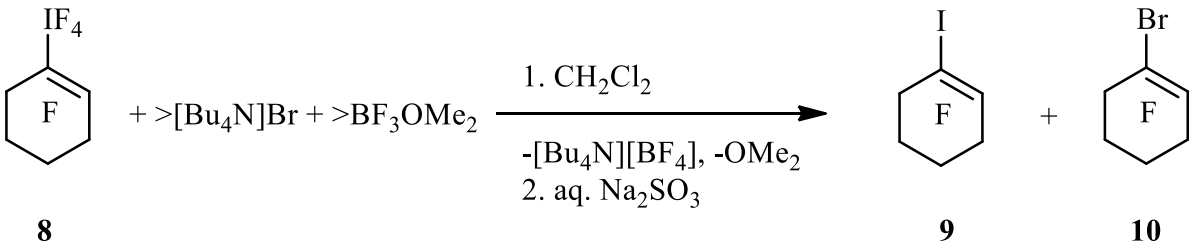
Scheme 6

To complete a picture, reactions of λ^5-iodanes **1**, **5** and **8** with halide anions in the presence of BF_3OMe_2 (fluoride anion acceptor) were investigated. Notably that these iodanes resist towards BF_3OMe_2 as well as the stronger Lewis acid, BF_3 [10]. It turned out that in these conditions, iodanes **1** and **5** were transformed into appropriate iodides. Other fluoroorganic products were absent (scheme 7).



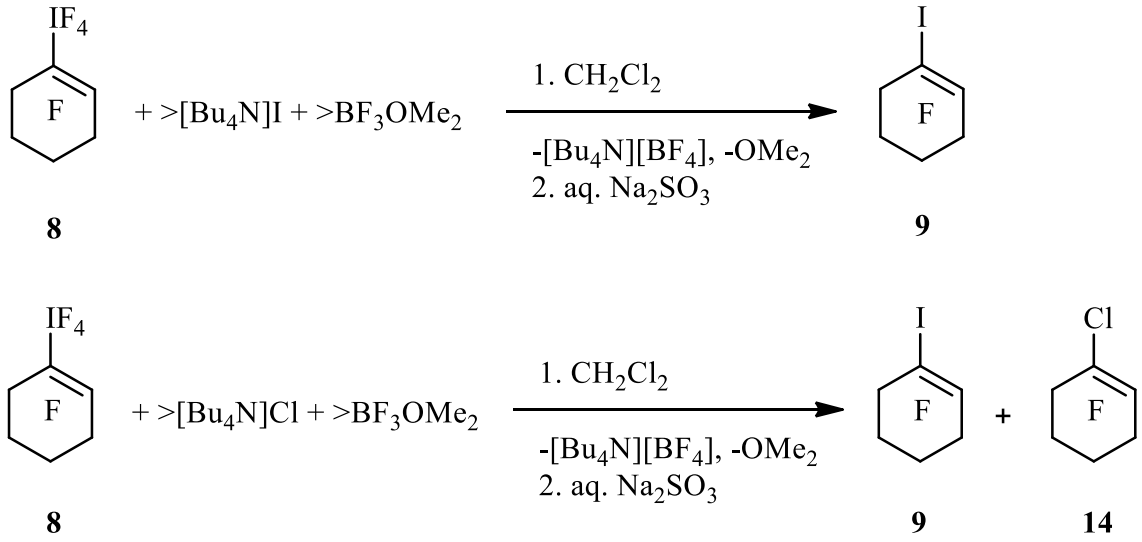
Scheme 7

Alternatively, iodane **8** formed mainly bromocyclohexene **10** while iodocyclohexene **9** was minor product (**9** : **10** = 1 : 9). Bromocyclohexane **11** (cf. scheme 4) was not found (scheme 8).



Scheme 8

Iodocyclohexene **9** was the only fluoroorganic product of reaction of **8** with $[Bu_4N]I$ and BF_3OMe_2. When **8** reacted with $[Bu_4N]Cl$ and BF_3OMe_2 that iodocyclohexene was formed together with admixture of 1-chlorononafluorocyclohexene (**14**) (scheme 9).



Scheme 9

The resulting picture shows that reactions of λ^5-iodanes R_FIF_4 with halides anions are not the simple reduction of I(V) but proceed several parallel channels. The contribution of each of them determines either by nature of halide and the constitution of perfluoroorganic moiety of iodane.

Experimental part

The ^{19}F NMR spectra were recorded on Bruker AVANCE 300 spectrometer at 282.40 MHz. The chemical shifts are referenced to 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 an internal quantitative standard 1,1,2-trichlorotrifluoroethane or C_6F_6. Products **2** [13], **3** [14, 15], **4** [16], **9**, **10**, **13, 14** [17], and **11** [18] were were identified by ^{19}F NMR spectroscopy.

Preparations of $C_6F_{13}IF_4$, $(CF_3)_2CFCF{=}CFIF_4$, 1-cyclo-$C_6F_9IF_4$, [10] and $[Me_4N]F$ [19], were described in literature. Dichloromethane (Baker), acetonitrile (Riedel-deHaën) were purified by standard procedures. $[Bu_4N]I$ (Merck), $[Bu_4N]Br$ (Fluka), $[Bu_4N]Cl$ (Fluka) were used as supplied. 1,1,1,3,3-Pentafluorobutane (PFB) (Solvay) was stored over molecular sieves 4A. All manipulations were performed in a FEP (block copolymer of tetrafluoroethylene and hexafluoropropylene) equipment under an atmosphere of dry argon.

Reaction of $C_6F_{13}IF_4$ **1** with $[Bu_4N]Br$

A. Solution of $C_6F_{13}IF_4$ (42 mg, 0.08 mmol) in PFB (0.4 ml) was added into stirred solution of $[Bu_4N]Br$ (142 mg, 0.44 mmol) in CH_2Cl_2 (0.7 ml). After 30 min, yellow solution was washed with 5% aq. Na_2SO_3, with water and dried with $MgSO_4$. The ^{19}F NMR spectrum showed the formation of $C_6F_{13}I$ (0.05 mmol), $C_6F_{13}Br$ (0.01 mmol) and $C_6F_{13}H$ (0.01 mmol).

B. $[Bu_4N]Br$ (780 mg, 2.4 mmol) was added in portions into cold (0 °C) stirred solution of $C_6F_{13}IF_4$ (208 mg, 0.40 mmol) and BF_3OMe_2 (124 mg, 1.08 mmol) in $CFCl_3$ (4 ml). Immediately red solution was formed. After 10 min the ^{19}F NMR spectrum showed the quantitative formation of 1-iodoperfluorohexane.

Reaction of $(CF_3)_2CFCF{=}CFIF_4$ **5** with $[Bu_4N]Br$

A. Cold (–15 °C) solution of $[Bu_4N]Br$ (317 mg, 0.98 mmol) in CH_2Cl_2 (1.0 ml) was added in portions into cold (–15 °C) solution of $(CF_3)_2CFCF{=}CFIF_4$ (*cis* : *trans* = 1 : 9) (104 mg, 0.24 mmol) in CH_2Cl_2 (0.7 ml) within 5 min. The immediately formed yellow solution was allowed to warm to 22 °C in 30 min, then it was washed with 5% aq. Na_2SO_3, with water and dried with $MgSO_4$. The ^{19}F NMR spectrum showed the formation of $(CF_3)_2CFCF{=}CFI$ (*cis* : *trans* = 1 : 9) (0.22 mmol) and *trans*-$(CF_3)_2CFCF{=}CFH$ (0.02 mmol).

B. Cold (–15 °C) solution of $[Bu_4N]Br$ (314 mg, 0.97 mmol) in CH_2Cl_2 (0.7 ml) was added in portions into cold (–15 °C) solution of $(CF_3)_2CFCF{=}CFIF_4$ (*cis* : *trans* = 1 : 9) (65 mg, 0.15 mmol) and BF_3OMe_2 (110 mg, 0.96 mmol) in CH_2Cl_2 (0.5 ml) within 5 min. The immediately formed red solution was allowed to warm to 22°C in 30 min. The ^{19}F NMR spectrum showed resonances of $(CF_3)_2CFCF{=}CFI$ (*cis* : *trans* = 1 : 9) (0.14 mmol), BF_3OMe_2 and $[Bu_4N][BF_4]$. After washing with 5% aq. Na_2SO_3, with water and drying with $MgSO_4$. yield of **6** and isomer ratio was not changed.

***trans*-1-Iodoperfluoro-4-methylbutene-1** (*trans*-**6**). ^{19}F NMR (CH_2Cl_2): δ = –76.3 (ddd, $^5J(F_3C, F^1)$ = 5 Hz, $^4J(F_3C, F^2)$ = 8 Hz, $^3J(F_3C, F^3)$ = 8 Hz, 6F, F_3C), –108.7 (ddsept, $^4J(F^1, F^3)$ = 40 Hz, $^3J(F^1, F^2)$ = 151 Hz, $^5J(F^1, F_3C)$ = 5 Hz,1F, F^1), –144.1 (ddsept, $^3J(F^2, F^3)$ = 15 Hz, $^3J(F^2, F^1)$ = 151 Hz, $^4J(F^2, F_3C)$ = 8 Hz, 1F, F^2), –187.4 (ddsept, $^3J(F^3, F^2)$ = 15 Hz, $^3J(F^3, F^1)$ = 40 Hz, $^3J(F^3, F_3C)$ = 8 Hz, 1F, F^3) (lit. [20] ^{19}F NMR (neat): δ = –75.4 (6F, F_3C), –108.5 (1F, F^1), –141.5 (1F, F^2), –186.0 (1F, F^3); $^4J(F^2, F_3C)$ = 8.9 Hz, $^5J(F^1, F_3C)$ = 4.7 Hz, $^3J(F_3C, F^3)$ = 13.2 Hz, $^4J(F^1, F^3)$ = 41.4 Hz, $^3J(F^1, F^2)$ = 148.8 Hz).

***cis*-1-Iodoperfluoro-4-methylbutene-1** (*cis*-**6**). ^{19}F NMR (CH_2Cl_2): δ = –75.7 (dd, $^3J(F_3C, F^3)$ = 9 Hz, $^4J(F_3C, F^2)$ = 9 Hz, 6F, F_3C), –83.5 (dd, $^4J(F^1, F^3)$ = 6 Hz, $^3J(F^1, F^2)$ = 10 Hz, 1F, F^1), –128.5 (m, 1F, F^2), –177.1 (dsept, $^4J(F^3, F^1)$ = 6 Hz, $^3J(F^3, F_3C)$ = 9 Hz, 1F, F^3).

Reaction of 1-cyclo-$C_6F_9IF_4$ **8** with $[Bu_4N]Br$

A. Solution of 1-cyclo-$C_6F_9IF_4$ (20 mg, 0.05 mmol) in CH_2Cl_2 (0.4 ml) was added into stirred solution of $[Bu_4N]Br$ (58 mg, 0.18 mmol) in CH_2Cl_2 (0.2 ml). The obtained solution contained 1-cyclo-C_6F_9I (0.015 mmol), 1-cyclo-C_6F_9Br (0.019 mmol) and bromoundecafluorocyclohexane (0.015 mmol) (^{19}F NMR). After washing with 5% aq. Na_2SO_3, with water and drying with $MgSO_4$. yields were not changed.

B. Solution of 1-cyclo-$C_6F_9IF_4$ (58 mg, 0.13 mmol) in CH_2Cl_2 (0.7 ml) was added into stirred solution of $[Bu_4N]Br$ (188 mg, 0.58 mmol) and BF_3OMe_2 (61 mg, 0.54 mmol) in CH_2Cl_2 (0.5 ml). After 15 min, red solution contained 1-cyclo-C_6F_9I (0.01 mmol), 1-cyclo-C_6F_9Br (0.10 mmol) beside $[Bu_4N][BF_4]$ (δ(F) = –151.0 ppm) (^{19}F NMR). Solution was washed with 5% aq. Na_2SO_3, with water and dried with $MgSO_4$. Yields of **9** and **10** were not changed (^{19}F NMR).

Reaction of 1-cyclo-$C_6F_9IF_4$ **8** with $[Bu_4N]Cl$ and BF_3OMe_2

Solution of 1-cyclo-$C_6F_9IF_4$ (58 mg, 0.13 mmol) in CH_2Cl_2 (0.7 ml) was added into stirred solution of $[Bu_4N]Cl$ (180 mg, 0.65 mmol) and BF_3OMe_2 (61 mg, 0.54 mmol) in CH_2Cl_2 (0.5 ml). After 15 min, yellow solution contained 1-iodononafluorocyclohexene (0.09 mmol) and 1-chlorononafluorocyclohexene (0.01 mmol) beside $[Bu_4N][BF_4]$ (^{19}F NMR).

Reaction of 1-cyclo-$C_6F_9IF_4$ **8** with $[Bu_4N]I$ and BF_3OMe_2

Solid $[Bu_4N]I$ (500 mg, 1.35 mmol) was added in portions into stirred solution of 1-cyclo-$C_6F_9IF_4$ (152 mg, 0.34 mmol) and BF_3OMe_2 (124 mg, 1.08 mmol) in CH_2Cl_2 (5 ml). Immediately iodine evolved and deep violet solution showed the presence of 1-cyclo-C_6F_9I and $[BF_4]^-$ (^{19}F NMR).

Solution was washed with 5% aq. Na_2SO_3, with water and dried with $MgSO_4$. The ^{19}F NMR spectrum contained resonances of 1-cyclo-C_6F_9I **9** (quantitative yield) and $[BF_4]^-$.

Reaction of 1-cyclo-$C_6F_9IF_4$ **8** with $[Me_4N]F$

Cold (–0 °C) solution of 1-cyclo-$C_6F_9IF_4$ (31 mg, 0.07 mmol) in CH_2Cl_2 (0.4 ml) was added into cold (–40 °C) stirred solution of $[Me_4N]F$ (18 mg, 0.19 mmol) in CH_2Cl_2 (0.2 ml). The reaction mixture was warmed to 22 °C over 20 min to form suspension. After 1 h white precipitate was separated by centrifugation from brownish mother liquor which contained only trace of fluoroorganic compounds (^{19}F NMR). Precipitate was separated by centrifugation, washed with dichloromethane and dried in vacuum to give white solid (32 mg). Freshly prepared solution in anhydrous MeCN contained **12**, **13**, $[Me_4N][IF_6]$ (singlet at 11.7 ppm [21]), and IF_5 (ratio 12:42:7:39) (^{19}F NMR). After 18 h at 22 ºC the ratio became 20:21:7:53.

Reaction of $[Me_4N][C_6F_{10}IF_4]$ **12** with bromine in MeCN

Cold (–15 °C) solution of bromine (20 mg, 0.125 mmol) in MeCN (0.08 ml) was added into cold (–15°C) solution of **12** in MeCN (see above). Salt **12** quantitatively converted to cyclohexenes **10** and **13** (3 : 7) (^{19}F NMR).

Reaction of 1-cyclo-$C_6F_9IF_4$ **8** with bromine and $[Me_4N]F$

Cold (–20 °C) solution of $[Me_4N]F$ (22 mg, 0.23 mmol) in CH_2Cl_2 (0.4 ml) was added into cold (–20 °C) stirred solution of 1-cyclo-$C_6F_9IF_4$ (31 mg, 0.07 mmol) and bromine (32 mg, 0.20 mmol) in CH_2Cl_2 (0.7 ml). Immediately white suspension formed. The reaction mixture was warmed to 22 °C over 10 min, and precipitate was separated by centrifugation. Yellow mother liquor contained cyclohexenes **10** (0.06 mmol) and **9** (trace). Solution of solid in CH_3CN contained $[Me_4N][IF_6]$ (^{19}F NMR).

Reaction of $C_6F_{13}IF_4$ **1** with $[Me_4N]F$

Cold (0 °C) solution of $[Me_4N]F$ (18 mg, 0.19 mmol) in EtCN (0.5 ml) was added into cold (–55 °C) stirred solution of **1**(66 mg, 0.12 mmol) in EtCN (0.6 ml). The reaction mixture was warmed to 22 °C over 6 h. Yellow solution contained $C_6F_{13}I$ (0.09 mmol), $C_6F_{13}H$ (trace) and unknown product $C_6F_{13}R$ ($R \neq IF_2$, IF_4) (^{19}F NMR).

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