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Journal of Fluorine Chemistry 99 (1999) 9–15

JOURNAL OF FLUORINE CHEMISTRY

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Synthesis and characterization of 2,6-difluorophenyliodine(III) derivatives

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Received 29 March 1999; accepted 7 May 1999

Dedicated to Prof. Friedo Huber on the occasion of his 70th birthday

Abstract

$2,6\text{-}F_2C_6H_3IF_2$ was isolated in quantitative yield from the reactions of $2,6\text{-}F_2C_6H_3I$ and XeF_2 or F_2/N_2-mixtures. Ligand exchange using $(CF_3CO)_2O$ gave the corresponding bis(trifluoroacetate) in 84% yield. The reaction of $2,6\text{-}F_2C_6H_3I(OCOCF_3)_2$ and $1,3\text{-}F_2C_6H_4$ in the presence of CF_3SO_3H selectively gave $[I(2,6\text{-}F_2C_6H_3)_2][OSO_2CF_3]$ in 80% yield.

Ligand exchange reactions of $2,6\text{-}F_2C_6H_3IF_2$ and triarylboranes in the presence of stoichiometric amounts of $BF_3{\cdot}O(CH_3)_2$ gave the corresponding 2,6-difluorophenyl(aryl)iodine(III) tetrafluoroborates in 45–85% yield.

Ligand exchange of the tetrafluoroborate was studied for some examples using $(CH_3)_3SiOSO_2CF_3$ or $(CH_3)_3SiOCOCF_3$ giving the corresponding 2,6-difluorophenyl(aryl)iodine(III) trifluoromethanesulfonates or trifluoroacetates in nearly quantitative yields.

All compounds were characterized by their NMR and mass spectra and melting and decomposition points.

Keywords: Fluorine; Iodine; 2,6-Difluorophenyliodine(III) compounds

1. Introduction

Aryliodine(III) derivatives have been known for more than a century [1] and have been the subject of several reviews [2,3] and monographs [4–6]. Fully fluorinated and partially fluorinated aryliodine(III) compounds have been synthesized by different routes, e.g.:

Ar_fIF_2: oxidative fluorination of fluoroiodobenzenes [7–10]; ligand exchange reactions of IF_3 and $Cd(C_6F_5)_2$ [11]; fluorination of C_6F_5IO using SF_4 [12].
$[IAr_f(Ar_f')]X$: oxidative arylation of iodobenzenes using $[XeAr_f]^+$ [13–15]; ligand exchange reactions on aryliodine difluorides [15] and iodine trifluoride [11] using triarylboranes; reaction of $C_6F_5SiF_3$ with $[IF_4][SbF_6]$ in FSO_3H [16]; electrophilic substitutions starting with $I(OCOCF_3)_3$ and a fluorobenzene in the presence of a strong acid, e.g. CF_3SO_3H [17].

Herein we report on the syntheses of a number of new aryliodine(III) compounds with the $2,6\text{-}F_2C_6H_3$-ligand (Scheme 1).

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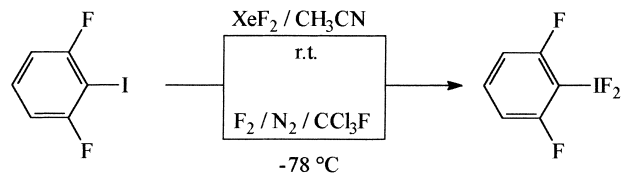
2. Results and discussion

2.1. Oxidation reactions of $2,6\text{-}F_2C_6H_3I$

$2,6\text{-}F_2C_6H_3IF_2$ was easily prepared from $2,6\text{-}F_2C_6H_3I$ either by direct fluorination or reaction with XeF_2. These oxidative fluorinations are comparable to the well-known syntheses of $C_6F_5IF_2$ [7,8].



$2,6\text{-}F_2C_6H_3IF_2$ was obtained in quantitative yield as a white solid melting at 164°C without decomposition and was chosen as starting material for the synthesis of a series of mono- and diaryliodine(III) derivatives.

2.2. Fluorine-trifluoroacetate exchange with $(CF_3CO)_2O$

$2,6\text{-}F_2C_6H_3IF_2$ was converted into $2,6\text{-}F_2C_6H_3I(OCOCF_3)_2$ with $(CF_3CO)_2O$ via the well-established method

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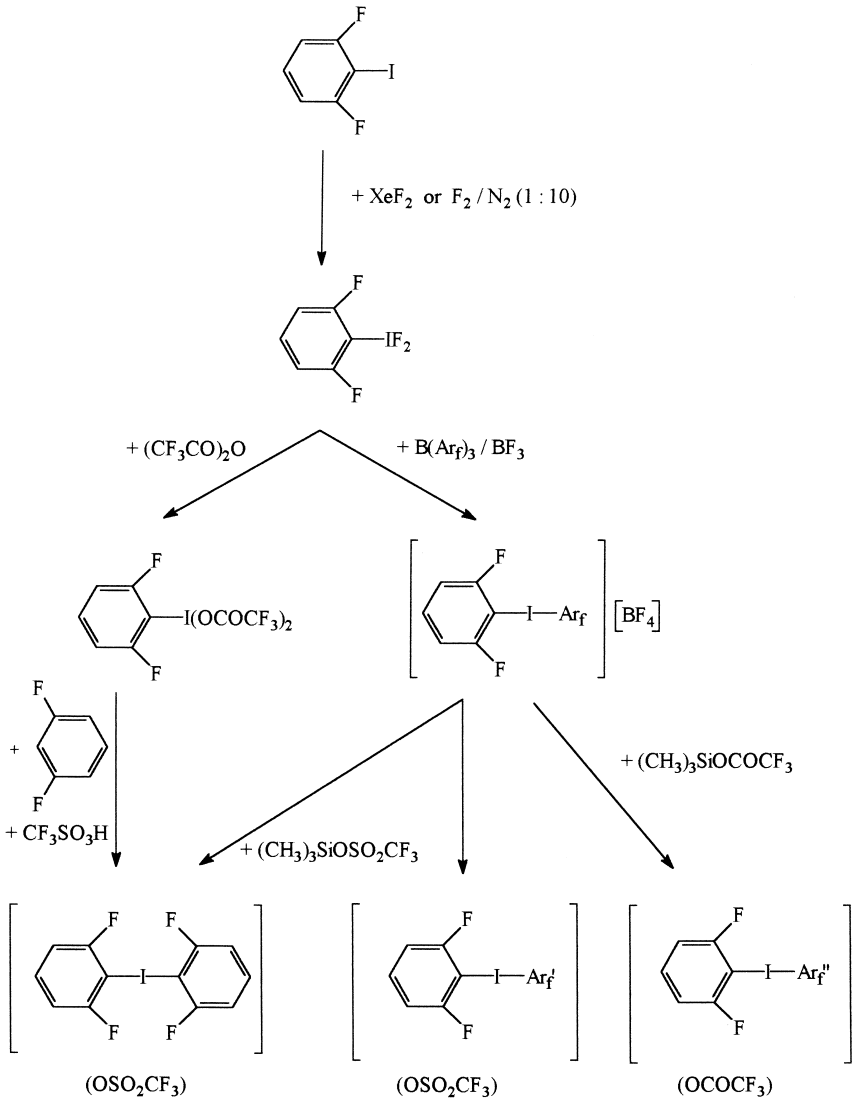


Ar_f = C_6F_5, 2,4,6-$F_3C_6H_2$, 2,6-$F_2C_6H_3$, 2-FC_6H_4, 3-FC_6H_4, 4-FC_6H_4
Ar_f' = 2,4,6-$F_3C_6H_2$, 4-FC_6H_4
Ar_f'' = 2,4,6-$F_3C_6H_2$, 2,6-$F_2C_6H_3$

Scheme 1. Survey of reactions.

for perfluoroorganoiodine(III) compounds [18]:

$$2,6\text{-}F_2C_6H_3IF_2 + 2(CF_3CO)_2O \rightarrow 2,6\text{-}F_2C_6H_3I(OCOCF_3)_2 + 2CF_3COF$$

2,6-$F_2C_6H_3I(OCOCF_3)_2$ was easily separated from volatile CF_3COF and excess $(CF_3CO)_2O$ and isolated in 85% yield as a white solid melting at 151°C.

2.3. Synthesis of diaryliodine trifluoromethanesulfonates via electrophilic aromatic substitution

The reaction of 2,6-difluorophenyliodine bis(trifluoroacetate) and 1,3-$F_2C_6H_4$ in the presence of trifluoromethanesulfonic acid gave bis(2,6-difluorophenyl)iodine trifluoromethanesulfonate, $[I(2,6\text{-}F_2C_6H_3)_2][OSO_2CF_3]$, in 80% yield. The process must be regarded as electrophilic aromatic substitution.

This synthetic approach has to be considered as a combination of two well known reactions described by Umemoto et al. [19] and our group [17]. This method had already been successfully applied to the synthesis of arylxenon(II) derivatives starting from $Xe(OCOCF_3)_2$ and fluorine, trifluoromethyl or nitro substituted benzenes in the presence of CF_3SO_3H or FSO_3H [20,21].

The reaction of 2,6-$F_2C_6H_3I(OCOCF_3)_2$ and 1,3-$F_2C_6H_4$ in the presence of CF_3SO_3H proceeded in CF_3COOH, and $[I(2,6\text{-}F_2C_6H_3)_2][OSO_2CF_3]$ was isolated after a reaction

time of 2 days as a pale yellow solid. Exact stoichiometry is necessary to avoid an incomplete reaction or the formation of unidentified by-products as observed using an excess of trifluoromethanesulfonic acid.

$$2,6\text{-}F_2C_6H_3I(OCOCF_3)_2 + 1,3\text{-}F_2C_6H_4 + CF_3SO_3H \rightarrow [I(2,6\text{-}F_2C_6H_3)_2]OSO_2CF_3 + 2CF_3COOH$$

In contrast, the reaction of $Xe(OCOCF_3)_2$ and 1,3-$F_2C_6H_4$ under similar conditions gave $[Xe(2,4\text{-}F_2C_6H_3)][OSO_2CF_3]$ as the major product [20,21]; however, no spectroscopic evidence was found for $[I(2,6\text{-}F_2C_6H_3)(2,4\text{-}F_2C_6H_3)][OSO_2CF_3]$ in reactions starting with 2,6-$F_2C_6H_3I(OCOCF_3)_2$. An explanation for this different reaction behaviour cannot be given.

2.4. Synthesis of diaryliodine(III) tetrafluoroborates starting from aryliodine difluorides and triarylboranes

Diaryliodine(III) tetrafluoroborates are accessible from reactions of aryliodine(III) difluorides and triarylboranes in the presence of stoichiometric amounts of $BF_3{\cdot}O(CH_3)_2$.

This method was earlier applied for the synthesis of $[I(C_6F_5)_2][BF_4]$ and the non-symmetrical species $[I(C_6F_5)(2,4,6\text{-}F_3C_6H_2)][BF_4]$ [14] by analogy to the reactions of XeF_2 and triarylboranes in the presence of $BF_3{\cdot}O(CH_3)_2$ to yield arylxenon(II) tetrafluoroborates [13,22–25].

Now we synthesized several compounds of the general formula $[I(2,6\text{-}F_2C_6H_3)Ar_f][BF_4]$ (Ar_f=C_6F_5, 2,4,6-$F_3C_6H_2$, 2,6-$F_2C_6H_3$, 2-FC_6H_4, 3-FC_6H_4, 4-FC_6H_4) according to

$$3(2,6\text{-}F_2C_6H_3)IF_2 + B(Ar_f)_3 + 2BF_3 \rightarrow 3[I(2,6\text{-}F_2C_6H_3)Ar_f][BF_4]$$

These reactions were performed in CH_2Cl_2 to precipitate the insoluble products. The addition of $BF_3{\cdot}O(CH_3)_2$ to the reaction mixtures supports the exclusive formation of salts with the tetrafluoroborate anion and avoids the formation of mixed arylfluoroborates. On the other hand the Lewis-acid BF_3 accelerates the reaction probably forming an adduct with 2,6-$F_2C_6H_3IF_2$ with simultaneous weakening of one I–F bond.

The remarkable stability of the diaryliodine(III) tetrafluoroborates is demonstrated by their decomposition points distinctly above 200°C. The high stability might be explained by delocalization of the positive charge on the aromatic ring systems [22].

2.5. Ligand exchange of the tetrafluoroborate anion using trimethylsilylesters of strong acids

$[I(2,6\text{-}F_2C_6H_3)_2][OSO_2CF_3]$ was also synthesized in an exchange reaction of the corresponding tetrafluoroborate, $[I(2,6\text{-}F_2C_6H_3)_2][BF_4]$, with $(CH_3)_3SiOSO_2CF_3$ in CH_3CN [26].

In extension of our previous work, trifluoromethanesulfonates and trifluoroacetates were prepared via exchange of the tetrafluoroborate anion using $(CH_3)_3SiOSO_2CF_3$ and $(CH_3)_3SiOCOCF_3$, respectively, with formation of the thermodynamically stable products $(CH_3)_3SiF$ and BF_3.

These reactions were exemplarily studied for some of the derivatives.

$$[I(2,6\text{-}F_2C_6H_3)Ar'_f][BF_4] + (CH_3)_3SiOSO_2CF_3 \rightarrow [I(2,6\text{-}F_2C_6H_3)Ar'_f][OSO_2CF_3] + (CH_3)_3SiF + BF_3$$

$$Ar'_f = 2,4,6\text{-}F_3C_6H_2, 4\text{-}FC_6H_4$$

$$[I(2,6\text{-}F_2C_6H_3)Ar''_f][BF_4] + (CH_3)_3SiOCOCF_3 \rightarrow [I(2,6\text{-}F_2C_6H_3)Ar''_f][OCOCF_3] + (CH_3)_3SiF + BF_3$$

$$Ar''_f = 2,6\text{-}F_2C_6H_3, 2,4,6\text{-}F_3C_6H_2$$

The exchange was complete in acetonitrile solution within 2–6 days. The products were isolated as stable pale yellow to white solids after distilling off all volatile components in vacuo.

2.6. Comparison of some properties of the new aryliodine(III) compounds

2.6.1. Thermal stability

All 2,6-difluorophenyliodine(III) compounds synthesized are stable solids. The melting and decomposition points are above 150°C and exhibit some interesting gradations depending on the groups attached to the 2,6-$F_2C_6H_3I$ unit.

In the series of different $[I(2,6\text{-}F_2C_6H_3)_2]$ salts thermal stability increases from the tetrafluoroborate (dec. p. 229°C) via the trifluoroacetate (dec. p. 288°C) to the trifluoromethanesulfonate (dec. p. > 350°C).

Within the group of mixed diaryliodine(III) tetrafluoroborates, $[I(2,6\text{-}F_2C_6H_3)(C_6F_5)][BF_4]$ is the most stable. The decomposition point of 322°C is about 100°C higher than the decomposition points of the other derivatives (Table 4).

2.6.2. Mass spectra

Some of the effects in thermal stability are consistent with effects observed in the mass spectrometric decay. Comparison of the mass spectra of 2,6-$F_2C_6H_3I(OCOCF_3)_2$, $[I(2,6\text{-}F_2C_6H_3)_2][OCOCF_3]$ and $[I(2,6\text{-}F_2C_6H_3)_2][OSO_2CF_3]$ exhibits in the case of the monoaryl compound the peak $[I(C_6H_3F_2)(OCOCF_3)]^+$ (m/e=353) as that of the highest mass.

The spectra of all $[I(2,6\text{-}F_2C_6H_3)_2]$ derivatives show the peak of the cation $[I(C_6H_3F_2)_2]^+$ ($m/e = 353$) and its fragments. In the cases of $[I(2,6\text{-}F_2C_6H_3)_2][OCOCF_3]$ and $[I(2,6\text{-}F_2C_6H_3)_2][BF_4]$ also fragment peaks of polymer units such as $[C_{24}H_9F_8I]^+$ ($m/e = 576$) and $[C_{18}H_7F_6I]^+$ ($m/e = 464$) were detected.

Whereas the trifluoromethanesulfonates show an easily explainable fragmentation [26], the decay of all but one

Table 1
NMR chemical shifts and $J(^{19}F–^{13}C)$ of 2,6-$F_2C_6H_3I$, 2,6-$F_2C_6H_3IF_2$ and 2,6-$F_2C_6H_3I(OCOCF_3)_2$ [a]

	2,6-$F_2C_6H_3I$	2,6-$F_2C_6H_3IF_2$	2,6-$F_2C_6H_3I$ $(OCOCF_3)_2$
^{19}F: δ(F-2,6)	−92.1	−95.9	−94.3
$\delta(IF_2)$	–	−164.6	–
$\delta(OCOCF_3)$	–	–	−73.6
^{1}H: δ(H-3,5)	6.85	7.37	7.34
δ(H-4)	7.28	7.79	7.79
^{13}C: δ(C-1)	71.3	107.9	102.6
$^{2}J(^{19}F–^{13}C)$	24	25	Broad
δ(C-2,6)	163.0	160.0	160.9
$^{1}J(^{19}F–^{13}C)$	246	255	256
$^{3}J(^{19}F–^{13}C)$	6	n.r.	n.r.
δ(C-3,5)	111.9	113.3	114.2
$^{2}J(^{19}F–^{13}C)$	25[a]	23	n.r.[b]
δ(C-4)	131.6	138.6	139.7
$^{3}J(^{19}F–^{13}C)$	10	10	10
δ(C=O)	–	–	161.1[c]
$\delta(CF_3)$	–	–	113.8[d]

δ in ppm, J in Hz. Solvents CD_3CN (^{1}H, ^{13}C) and CH_3CN (^{19}F), external lock $(CD_3)_2CO$). n.r. = not resolved.
[a] $^{4}J(^{19}F–^{13}C) = 3$ Hz.
[b] Signals overlap.
[c] $^{2}J(^{19}F–^{13}C) = 40.2$ Hz.
[d] $^{1}J(^{19}F–^{13}C) = 287.0$ Hz.

derivatives of the general formula $[I(2,6\text{-}F_2C_6H_3)Ar_f][BF_4]$ was similar. They decompose under mass spectrometric conditions with formation of fragments in intensities mainly less than 10% which could be interpreted as polyphenyliodine ions.

Only $[I(2,6\text{-}F_2C_6H_3)(C_6F_5)][BF_4]$ showed a fragmentation pattern comparable with the trifluoromethanesulfonates. Besides the cation peak ($m/e = 407$) the fragments $[C_6F_5I]^+$, $[C_6H_3F_2I]^+$, $[C_6HF_5]^+$, $[C_6H_3F_3]^+$ and $[C_6H_3F_2]^+$ were detected. The ion of highest mass was $[I(C_6H_3F_2)(C_6F_5)F]^+$ ($m/e = 426$).

2.6.3. NMR spectra

A comparison of the NMR chemical shifts of 2,6-$F_2C_6H_3I$, 2,6-$F_2C_6H_3IF_2$ and 2,6-$F_2C_6H_3I(OCOCF_3)_2$ (Table 1) exhibits characteristic alteration with the change of the iodine oxidation state from I to III. At comparable conditions, the F-2,6-resonance is shifted approximately 2–4 ppm to higher field; high-field shifts of ca. 0.5 ppm are found for all proton resonances. Significant low-field shifts are measured for the C-1-atom (up to 36.6 ppm) and the C-4-atom (up to 8.1 ppm); the shifts of the C-2,6- and C-3,5-atoms remain nearly unaffected by the change of oxidation states.

The NMR chemical shifts of the 2,6-$F_2C_6H_3$-group of the diaryl derivatives are neither influenced by different anions nor different fluorophenyl groups attached to the iodine center (Tables 3 and 4). However, the C-1 chemical shifts of $[I(2,6\text{-}F_2C_6H_3)Ar_f]^+$ and 2,6-$F_2C_6H_3IX_2$ (X = F, $OCOCF_3$) differ by ca. 17 and 12 ppm, respectively.

3. Experimental

All reactions were carried out in carefully dried reaction vessels using Schlenk-techniques. 2,6-$F_2C_6H_3I$, 1,3-$F_2C_6H_4$ and CF_3SO_3H (freshly distilled) were purchased from ABCR, $(CH_3)_3SiOCOCF_3$ and $(CH_3)_3SiOSO_2CF_3$ from Aldrich, $BF_3{\cdot}O(CH_3)_2$ from Merck-Schuchardt and used as received. Elemental fluorine, CF_3COOH and $(CF_3CO)_2O$ were received from Solvay Fluor und Derivate as gifts. $B(Ar_f)_3$ and XeF_2 were prepared according to literature procedures [27] and [28], respectively. All solvents were purified by standard methods [29].

NMR spectra were recorded on Bruker FT-NMR spectrometers AC 200 and AMX 300 operating at 200.1 MHz (300.1 MHz) [^{1}H], 188,3 MHz (282.4 MHz) [^{19}F] and 50.3 MHz (75.5 MHz) [^{13}C]. CCl_3F [^{19}F] and $(CH_3)_4Si$ [^{1}H, ^{13}C] were used as external standards.

Mass spectra were run on a modified Varian MAT CH5 spectrometer, DTA measurements on a Mettler TA1 thermoanalyzer.

3.1. Synthesis of 2,6-$F_2C_6H_3IF_2$

3.1.1. Fluorination of 2,6-$F_2C_6H_3I$ with XeF_2

1.0 g (4.1 mmol) 2,6-$F_2C_6H_3I$ were dissolved in 5 ml CH_3CN. A solution of 0.7 g (4.1 mmol) XeF_2 in 5 ml CH_3CN was added dropwise. After stirring the reaction mixture for 24 h at room temperature, the solvent was distilled off in vacuo. 2,6-$F_2C_6H_3IF_2$ was obtained as a white solid in quantitative yield.

3.1.2. Fluorination of 2,6-$F_2C_6H_3I$ with F_2

4.0 g (16.4 mmol) 2,6-$F_2C_6H_3I$ were suspended in 60 ml CCl_3F. A precooled fluorine-gasflow diluted with nitrogen (1 : 10) was bubbled through the solution. After a few minutes a white solid began to precipitate. The reaction was stopped as soon as elemental fluorine passed through the reaction vessel without further reaction. After distilling off the solvent in vacuo at room temperature 2,6-$F_2C_6H_3IF_2$ was obtained as a white solid in quantitative yield.

m.p. 164°C, dec. 185°C. MS (EI, 20 eV, 100°C; *m/e*): 278 (5%, $[F_2C_6H_3IF_2]^+ = M^+$), 259 (8%, $[F_2C_6H_3IF]^+$), 240 (100%, $[F_2C_6H_3I]^+$), 132 (62%, $[F_3C_6H_3]^+$), 113 (44%, $[F_2C_6H_3]^+$).

NMR data are summarized in Table 1.

3.2. Synthesis of 2,6-$F_2C_6H_3I(OCOCF_3)_2$

1.4 g (5.0 mmol) 2,6-$F_2C_6H_3IF_2$ was suspended in 10 ml $(CF_3CO)_2O$. After stirring the reaction mixture for 48 h at room temperature, all volatile components, mainly $(CF_3CO)_2O$ and CF_3COF, were distilled off in vacuo. 2,6-$F_2C_6H_3I(OCOCF_3)_2$ was obtained as a white solid in 85% (1.98 g) yield.

m.p. 151°C, Sublimation: 110°C at 10^{-3} bar. MS (EI, 17 eV, 90°C; *m/e*): 353 (71%, $[I(F_2C_6H_3)(OCOCF_3)]^+$), 240

(100%, $[F_2C_6H_3I]^+$), 226 (53%, $[F_2C_6H_3OCOCF_3]^+$ or $[(F_2C_6H_3)_2]^+$), 113 (39%, $[F_2C_6H_3]^+$ or $[CF_3CO_2]^+$).

NMR data are summarized in Table 1.

Elemental analysis for $C_{10}H_3F_8IO_4$ [found (calculated)] I: 26.7 (27.3)%; F: 33.4 (32.6)%.

3.3. Synthesis of $[I(2,6\text{-}F_2C_6H_3)_2][OSO_2CF_3]$

1.1 g (2.4 mmol) 2,6-$F_2C_6H_3I(OCOCF_3)_2$ was suspended in 20 ml CF_3COOH at 0°C and 0.22 ml (2.4 mmol) 1,3-$F_2C_6H_4$ were added. After stirring for 1 h and adding 0.21 ml (2.4 mmol) CF_3SO_3H, the reaction mixture was allowed to warm up to room temperature and stirred for an additional 48 h. All volatile compounds were distilled off in vacuo. $[I(2,6\text{-}F_2C_6H_3)_2][OSO_2CF_3]$ remained as a pale yellow solid in 80% (0.96 g) yield.

The analytical data corresponded with those given in [26].

3.4. Synthesis of $[I(2,6\text{-}F_2C_6H_3)(Ar_f)][BF_4]$ ($Ar_f = C_6F_5$, 2,4,6-$F_3C_6H_2$, 2,6-$F_2C_6H_3$, 2-FC_6H_4, 3-FC_6H_4, 4-FC_6H_4)

General procedure: 0.83 g (3.0 mmol) 2,6-$F_2C_6H_3IF_2$ were dissolved in 10 ml CH_2Cl_2 at −40°C. A precooled mixture (−40°C) of the corresponding borane (ca. 1.0 mmol) and 0.19 ml (2.07 mmol) $BF_3{\cdot}O(CH_3)_2$ in 20 ml CH_2Cl_2 were added dropwise. After 1 h the solution had taken on a brown colour from which a white solid began to precipitate. For completion of the reaction, the mixture was stirred for additional 24 h. The solid was filtered off at −40°C and washed with cold CH_2Cl_2. After drying the residue in vacuo, the diaryliodine tetrafluoroborates were obtained as white solids.

NMR data are summarized in Tables 2 and 3, experimental details, melting and decomposition points in Table 4.

3.4.1. Mass spectra

$[I(2,6\text{-}F_2C_6H_3)_2][BF_4]$ (EI, 15 eV, 190°C; *m/e*): 686 (7%, $[C_{30}H_9F_{10}I]^+$), 574 (8%, $[C_{24}H_7F_8I]^+$), 463 (8%, $[C_{18}H_6F_6I]^+$), 351 (12%, $[C_{12}H_4F_4I]^+$), 239 (100%, $[C_6H_2F_2I]^+$), 127 (2%, $[I]^+$), 113 (24%, $[C_6H_3F_2]^+$).

$[I(2,6\text{-}F_2C_6H_3)(C_6F_5)][BF_4]$ (EI, 17 eV, 60°C; *m/e*): 426 (15%, $[I(C_6H_3F_2)(C_6F_5)F]^+$), 407 (31%, $[I(C_6H_3F_2)\text{-}(C_6F_5)]^+$), 294 (74%, $[C_6F_5I]^+$), 240 (98%, $[C_6H_3F_2I]^+$), 168 (20%, $[C_6HF_5]^+$), 132 (100%, $[C_6H_3F_3]^+$), 113 (11%, $[C_6H_3F_2]^+$).

$[I(2,6\text{-}F_2C_6H_3)(2,4,6\text{-}F_3C_6H_2)][BF_4]$ (EI, 17 eV, 180°C; *m/e*): 500 (4%, $[C_{18}H_5F_8I]^+$), 482 (5%, $[C_{18}H_6F_7I]^+$), 370 (9%, $[C_{12}H_4F_5I]^+$), 352 (3%, $[C_{12}H_5F_4I]^+$), 258 (86%, $[C_6H_2F_3I]^+$), 240 (100%, $[C_6H_3F_2I]^+$).

$[I(2,6\text{-}F_2C_6H_3)(2\text{-}FC_6H_4)][BF_4]$ (EI, 15 eV, 175°C; *m/e*): 352 (3%, $[C_{12}H_5F_4I]^+$), 334 (5%, $[C_{12}H_6F_3I]^+$), 240 (100%, $[C_6H_3F_2I]^+$), 222 (44%, $[C_6HFI]^+$), 114 (11% $[C_6H_4F_2]^+$), 96 (3%, $[C_6H_5F]^+$).

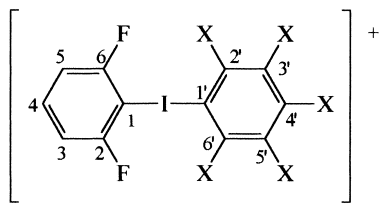
$[I(2,6\text{-}F_2C_6H_3)(3\text{-}FC_6H_4)][BF_4]$ (EI, 15 eV, 150°C; *m/e*): 352 (2%, $[C_{12}H_5F_4I]^+$), 334 (5%, $[C_{12}H_6F_3I]^+$), 240 (100%, $[C_6H_3F_2I]^+$), 222 (28%, $[C_6H_4FI]^+$), 113 (13%, $[C_6H_3F_2]^+$), 95 (12%, $[C_6H_4F]^+$).

$[I(2,6\text{-}F_2C_6H_3)(4\text{-}FC_6H_4)][BF_4]$ (EI, 15 eV, 160°C; *m/e*): 446 (3%, $[C_{18}H_8F_5I]^+$), 352 (5%, $[C_{12}H_5F_4I]^+$), 334 (5%, $[C_{12}H_6F_3I]^+$), 240 (100%, $[C_6H_3F_2I]^+$), 222 (87%, $[C_6H_4FI]^+$), 114 (25%, $[C_6H_4F_2]^+$), 95 (24%, $[C_6H_4F]^+$).

3.5. Synthesis of $[I(2,6\text{-}F_2C_6H_3)(2,4,6\text{-}F_3C_6H_2)][OSO_2CF_3]$ and $[I(2,6\text{-}F_2C_6H_3)(2\text{-}FC_6H_4)][OSO_2CF_3]$

General procedure: The corresponding diaryliodine tetrafluoroborate ($[I(2,6\text{-}F_2C_6H_3)(2,4,6\text{-}F_3C_6H_2)][BF_4]$ 0.77 g (1.7 mmol); $[I(2,6\text{-}F_2C_6H_3)(4\text{-}FC_6H_4)][BF_4]$ 0.14 g (0.3 mmol)) was dissolved in 10 ml CH_3CN and stoichiometric amounts of $(CH_3)_3SiOSO_2CF_3$ dissolved in 10 ml CH_3CN were added dropwise to the solution at −40°C.

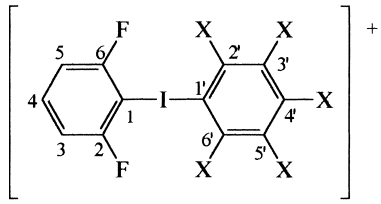
Table 2
^{19}F-NMR chemical shifts of 2,6-difluorophenyl(fluorophenyl)iodine(III) tetrafluoroborates[a]



	δ(F-2,6)	δ(F-2′)	δ(F-3′)	δ(F-4′)	δ(F-5′)	δ(F-6′)	δ($[BF_4]^-$)
$[I(2,6\text{-}F_2C_6H_3)(C_6F_5)]^+$	−94.5	−121.6	−156.4	−142.7	−156.4	−121.6	−149.0
$[I(2,6\text{-}F_2C_6H_3)(2,4,6\text{-}F_3C_6H_2)]^+$	−94.6	−91.6		−95.3		−91.6	−149.5
$[I(2,6\text{-}F_2C_6H_3)_2]^+$	−94.9						−150.4
$[I(2,6\text{-}F_2C_6H_3)(2\text{-}FC_6H_4)]^+$	−95.3	−96.0					−150.0
$[I(2,6\text{-}F_2C_6H_3)(3\text{-}FC_6H_4)]^+$	−94.9		−106.1				−149.9
$[I(2,6\text{-}F_2C_6H_3)(4\text{-}FC_6H_4)]^+$	−95.3			−104.1			−150.2

[a] Solvent CH_3CN, external lock $(CD_3)_2CO$, δ in ppm.

Table 3
$^{13}C\{^{1}H\}$-NMR chemical shifts of 2,6-difluorophenyl(fluorophenyl)iodine(III) tetrafluoroborates[a]



	δ(C-1)	δ(C-2,6)	δ(C-3,5)	δ(C-4)	δ(C-1′)	δ(C-2′)	δ(C-′3)	δ(C-4′)	δ(C-5′)	δ(C-6′)
$[I(2,6\text{-}F_2C_6H_3)(C_6F_5)]^+$	91.2	161.6	114.2	140.1	87.4	147.5	138.6	147.3	138.6	147.5
$[I(2,6\text{-}F_2C_6H_3)(2,4,6\text{-}F_3C_6H_2)]^+$	90.7	161.7	114.2	139.8	86.2	162.7	103.7	168.9	103.7	162.7
$[I(2,6\text{-}F_2C_6H_3)_2]^+$	90.1	161.3	113.8	139.3						
$[I(2,6\text{-}F_2C_6H_3)(2\text{-}FC_6H_4)]^+$	90.3	161.5	114.1	139.4	100.6	160.6	118.5	137.9	128.9	138.6
$[I(2,6\text{-}F_2C_6H_3)(3\text{-}FC_6H_4)]^+$	90.4	161.6	114.3	139.4	112.9	124.0	163.3	121.8	134.8	133.0
$[I(2,6\text{-}F_2C_6H_3)(4\text{-}FC_6H_4)]^+$	90.6	161.5	114.1	139.2	107.6	139.6	120.5	166.1	120.5	139.6

Solvent CD_3CN, δ in ppm.

After a total reaction time of 48 h all volatile compounds were distilled off in vacuo until a pale yellow residue remained. The yields were quantitative. No melting was observed up to the decomposition point of 350°C.

The ^{1}H- and ^{19}F-NMR data for the aromatic rings were identical with those of the corresponding tetrafluoroborates. The resonance of the CF_3SO_3 group was detected at −78.8 ppm in the ^{19}F-NMR spectra and at 121.3 ppm ($^{1}J(^{19}F-^{13}C) = 319$ Hz) in the ^{13}C-NMR spectra.

3.6. Synthesis of $[I(2,6\text{-}F_2C_6H_3)_2][OCOCF_3]$

0.97 g (2.2 mmol) $[I(2,6\text{-}F_2C_6H_3)_2][BF_4]$ were suspended in 10 ml CH_3CN at 0°C. A precooled solution of 0.41 ml (2.2 mmol) $(CH_3)_3SiOCOCF_3$ in 10 ml CH_3CN (0°C) was added dropwise and the mixture was stirred for 6 days at this temperature. After distilling off all volatile components in vacuo at room temperature $[I(2,6\text{-}F_2C_6H_3)_2][OCOCF_3]$ was isolated as a white solid in 95% (0.98 g) yield.

Dec. 288°C. MS (EI, 15 eV, 175°C; *m/e*): 576 (4%, $[C_{24}H_9F_8I]^+$), 464 (9%, $[C_{18}H_7F_6I]^+$), 353 (16%, $[C_{12}H_6F_4I]^+$), 240 (100%, $[C_6H_3F_2I]^+$), 226 (4%, $[F_2C_6H_3OCOCF_3]^+$ or $[(F_2C_6H_3)_2]^+$), 113 (8%, $[F_2C_6H_3]^+$ or $[CF_3CO_2]^+$). ^{1}H-NMR (CD_3CN): δ: 7.80 (H-4), 7.31 (H-3,5). ^{19}F-NMR (CD_3CN): δ: −75.9 (CF_3), −94.5 (F-2,6). $^{13}C\{^{19}F\}$-NMR (CD_3CN): δ: 161.9 (C-2,6), 157.8 (C=O), 139.8 (C-4), 116.6 (CF_3), 114.3 (C-3,5), 90.6 (C-1).

Elemental analysis for $C_{14}H_6F_7IO_2$: [found (calculated)] I: 27.68 (27.25)%; F, 28.18 (28.54)%.

3.7. Synthesis of $[I(2,6\text{-}F_2C_6H_3)(2,4,6\text{-}F_3C_6H_2)][OCOCF_3]$

0.38 g (0.83 mmol) $[I(2,6\text{-}F_2C_6H_3)(2,4,6\text{-}F_3C_6H_2)][BF_4]$ was dissolved in 5 ml CH_3CN and a solution of 0.14 ml (0.80 mmol) $(CH_3)_3SiOCOCF_3$ was added slowly at 0°C. After a reaction time of 4 days at room temperature the solvent and other volatile products were distilled off. $[I(2,6\text{-}F_2C_6H_3)(2,4,6\text{-}F_3C_6H_2)][OCOCF_3]$ was isolated as a white solid.

Dec. >300°C. MS (EI, 20 eV, 175°C; *m/e*): 594 (1%, $[C_{24}H_8F_9I]^+$), 500 (4%, $[C_{18}H_5F_8I]^+$), 482 (4%, $[C_{18}H_6F_7I]^+$), 464 (1%, $[C_{18}H_7F_6I]^+$), 388 (2%, $[C_{12}H_3F_6I]^+$), 370 (5%, $[C_{12}H_4F_5I]^+$), 352 (2%, $[C_{12}H_5F_4I]^+$), 338 (2%, $[C_{18}H_8F_6]^+$), 258 (42%, $[C_6H_2F_3I]^+$), 240 (35%, $[C_6H_3F_2I]^+$), 226 (2%, $[F_2C_6H_3OCOCF_3]^+$ or $[(F_2C_6H_3)_2]^+$), 131 (20%, $[C_6H_2F_3]^+$), 113 (20%, $[F_2C_6H_3]^+$ or $[CF_3CO_2]^+$).

^{19}F-NMR (CH_3CN): δ: −76.6 (CF_3), −91.9 (F-2,6 in 2,4,6-$F_3C_6H_2$ group), −94.9 (F-2,6 in 2,6-$F_2C_6H_3$), −95.6 (F-4 in 2,4,6-$F_3C_6H_2$ group).

Table 4
Melting points, decomposition points and experimental details for the synthesis of $[I(2,6\text{-}F_2C_6H_3)Ar_f][BF_4]$ from $2,6\text{-}F_2C_6H_3IF_2$ and $B(Ar_f)_3/BF_3{\cdot}O(CH_3)_2$[a]

Ar_f	C_6F_5	2,4,6-$F_3C_6H_2$	2,6-$F_2C_6H_3$	2-FC_6H_4	3-FC_6H_4	4-FC_6H_4
m ($2,6\text{-}F_2C_6H_3IF_2$)	0.83 g [2.99]	0.83 g [2.99]	0.83 g [2.99]	0.83 g [2.99]	0.83 g [2.99]	0.83 g [2.99]
m ($B(Ar_f)_3$)	0.51 g [1.00]	0.40 g [0.99]	0.35 g [1.00]	0.30 g [1.01]	0.30 g [1.01]	0.30 g [1.01]
m ($BF_3{\cdot}O(CH_3)_2$)	0.19 ml [2.07]	0.19 ml [2.07]	0.19 ml [2.07]	0.19 ml [2.07]	0.19 ml [2.07]	0.19 ml [2.07]
Yield	0.66 g (45%)	0.75 (55%)	1.12 g (85%)	0.88 g (70%)	0.63 g (50%)	0.59 g (47%)
Melting point	272°C			194°C	176°C	167°C
Dec. point	322°C	208°C	229°C	219°C	222°C	225°C

[a]Amounts in mmol are given in square brackets. Yields are referenced to $2,6\text{-}F_2C_6H_3IF_2$.

Acknowledgements

Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged.

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