

The first perfluoro alkyl(aryl)iodonium salt synthesised on two complementary routes

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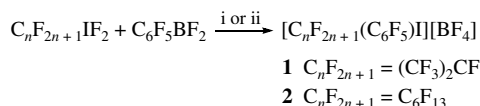
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The first representatives of the previously unknown perfluoroalkyl(perfluoroaryl)iodonium salts $[C_nF_{2n+1}(Ar_F)I]Y$ were prepared by reaction of perfluorinated alkyl iodine difluorides $C_nF_{2n+1}IF_2$ with aryldifluoroborane $C_6F_5BF_2$ and on the complementary route from perfluorinated aryl iodine difluoride $C_6F_5IF_2$ and alkyl difluoroborane $C_6F_{13}BF_2$.

In contrast to aryl(perfluoroalkyl)iodonium salts,¹ which are known for more than two decades and widely applied for electrophilic perfluoroalkylation reactions in organic synthesis, their perfluorinated analogues, as well as any perfluoroalkyl(perfluoroaryl)iodonium salt $[C_nF_{2n+1}(R_F)I]Y$, are still unknown.² Here, we report two effective routes to perfluoro alkyl(aryl)iodonium salts. Both routes have in common the use of perfluoro organyl iodine difluorides R_FIF_2 ² and organyl difluoroboranes R'_FBF_2 ³ ($R_F, R'_F = C_nF_{2n+1}$ or C_6F_5).

The route to $[C_nF_{2n+1}(C_6F_5)I][BF_4]$ salts is based on the addition of $C_6F_5BF_2$ to a solution of $C_nF_{2n+1}IF_2$ [†] at low temperatures in weakly coordinating, strictly dry solvents, such as CH_2Cl_2 , CCl_3F and 1,1,1,3,3,3- $C_3H_3F_5$. The salts can be easily isolated after removal of all volatiles in a vacuum. Note that iodonium salts with both linear and branched alkyl groups can be obtained[‡] (Scheme 1).

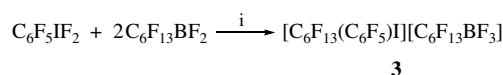


Scheme 1 Reagents and conditions: i (1), CH_2Cl_2 , $-40^\circ C$; ii (2), CCl_3F , $0^\circ C$.

[†] $(CF_3)_2CFIF_2$. A cold fluorine–nitrogen gas mixture (3 vol%), passed through a $-78^\circ C$ copper coil) was introduced into a cold ($-78^\circ C$) stirred solution of $(CF_3)_2CFI$ (1.05 g, 3.55 mmol) in CCl_3F (6 ml) until F_2 was detected at the outlet (wet KI indicator paper). The white product suspension was centrifuged at $-78^\circ C$, and the precipitate was dried in a vacuum at $-40^\circ C$. The raw product $(CF_3)_2CFIF_2$ (80–85% yield) contained $(CF_3)_2CFI$, IF_3 and $(CF_3)_2CFIF_4$ (total 4–5%). Pure product was obtained by crystallization from CCl_3F : mp 39–41 $^\circ C$. ^{19}F NMR (CH_2Cl_2) δ : -71.4 [dt, 6F, 2CF₃, $^3J_{F(2)-F(1)}$ 8 Hz, $^4J_{F(2)-IF}$ 8 Hz], -140.4 [sept., 1F, F(1), $^3J_{F(1)-F(2)}$ 8 Hz], -169.2 [sept., 2F, IF₂, $^4J_{IF-F(2)}$ 8 Hz]. ^{19}F NMR (CD_3CN) δ : -70.3 [dt, 6F, 2CF₃, $^3J_{F(2)-F(1)}$ 8 Hz, $^4J_{F(2)-IF}$ 8 Hz], -145.9 [sept., 1F, F(1), $^3J_{F(1)-F(2)}$ 8 Hz], -171.1 [sept., 2F, IF₂, $^4J_{IF-F(2)}$ 8 Hz].

$C_6F_{13}IF_2$. It was prepared by analogy to $(CF_3)_2CFIF_2$ in 84% yield from $C_6F_{13}I$ (2.05 g, 4.6 mmol) in CCl_3F (10 ml). The crude product was washed with a small volume of CCl_3F at $-78^\circ C$, crystallized from CCl_3F and dried in a vacuum at $-40^\circ C$: mp 53–55 $^\circ C$ (lit.,⁶ 35 $^\circ C$). ^{19}F NMR (CH_2Cl_2) δ : -75.6 [s, 2F, F(1)], -81.3 [m, 3F, F(6)], -116.9 [m, 2F, F(2)], -121.6 [m, 2F, F(3)], -122.8 [m, 2F, F(4)], -126.4 [m, 2F, F(5)], -171.6 [s, 2F, IF₂, $\tau_{1/2}$ = 38 Hz]. ^{19}F NMR (CD_3CN , $-40^\circ C$) δ : -80.3 [t, 3F, F(6), $^4J_{F(6)-F(4)}$ 10 Hz], -81.8 [m, 2F, F(1)], -117.4 [m, 2F, F(2)], -121.3 [m, 2F, F(3)], -122.3 [m, 2F, F(4)], -125.8 [m, 2F, F(5)], -173.3 [s, 2F, IF₂, $\tau_{1/2}$ = 27 Hz].

The availability of the complementary route to $[C_nF_{2n+1}(C_6F_5)I]Y$ salts from $C_6F_5IF_2$ and $C_nF_{2n+1}BF_2$ was not *a priori* promising because of the weak nucleophilicity of the perfluoroalkyl group, which has to migrate from boron to iodine(III). Surprisingly, this reaction according to Scheme 2 occurs with 2 equiv. of perfluorohexyldifluoroborane and results in the desired iodonium cation with the corresponding perfluoroalkyltrifluoroborate anion in a good yield[§] (Scheme 2).



Scheme 2 Reagents and conditions: i, 1,1,1,3,3-pentafluoropropane (PFP), $-40^\circ C$.

[‡] A solution of $C_6F_5BF_2$ (129 mg, 0.60 mmol) in CH_2Cl_2 (2 ml) was added in portions to the stirred cold ($-50^\circ C$) solution of $(CF_3)_2CFIF_2$ (201 mg, 0.60 mmol) in CH_2Cl_2 (1 ml). After 1 h, the precipitate was separated by centrifugation and washed with cold ($-50^\circ C$) CH_2Cl_2 (0.4 ml). $[(CF_3)_2CF(C_6F_5)I][BF_4]$ **1** was obtained as a colourless solid in ~80% yield after drying in a vacuum at $-40^\circ C$. ^{19}F NMR (MeCN, $-40^\circ C$) δ : -70.9 [d, 6F, F(2), $^3J_{F(2)-F(1)}$ 12 Hz], -118.9 [m, 2F, *o*-F], -136.3 [tt, 1F, *p*-F, $^3J_{p-F-m-F}$ 21 Hz, $^4J_{p-F-o-F}$ 9 Hz], -138.9 [sept., 1F, F(1), $^3J_{F(1)-F(2)}$ 12 Hz], -146.7 [s, 4F, $[BF_4]^-$], -154.0 [m, 2F, *m*-F].

A solution of $C_6F_5BF_2$ (38 mg, 0.17 mmol) in CCl_3F (1 ml) was added in portions to the stirred cold ($0^\circ C$) solution of $C_6F_{13}IF_2$ (89 mg, 0.18 mmol) in CCl_3F (0.5 ml). After a few minutes, the yellowish solution was evaporated to dryness at $0^\circ C$ in a vacuum, and the solid residue was washed with CCl_3F until CCl_3F became colourless. After drying in a vacuum at $0^\circ C$, $[C_6F_{13}(C_6F_5)I][BF_4]$ **2** was isolated as a colourless solid in > 90% yield. ^{19}F NMR (CD_3CN , $-40^\circ C$) δ : -62.2 [m, 2F, F(1)], -80.6 [t, 3F, F(6), $^4J_{F(6)-F(4)}$ 10 Hz], -113.8 [m, 2F, F(2)], -119.4 [m, 2F, *o*-F], -121.2 [m, 2F, F(3)], -122.4 [m, 2F, F(4)], -126.1 [m, 2F, F(5)], -138.3 [tt, 1F, *p*-F, $^3J_{p-F-m-F}$ 20 Hz, $^4J_{p-F-o-F}$ 8 Hz], -147.1 [s, 4F, $[BF_4]^-$], -154.9 [m, 2F, *m*-F]. ^{13}C NMR (CD_3CN , $-25^\circ C$) δ : 148.3 [ddt, C(4), $^1J_{C(4)-p-F}$ 263 Hz, $^2J_{C(4)-m-F}$ 13 Hz, $^3J_{C(4)-o-F}$ 6 Hz], 147.9 [dm, C(2), C(6), $^1J_{C(2), C(6)-o-F}$ 250 Hz], 138.9 [dm, C(3), C(5), $^1J_{C(3), C(5)-m-F}$ 258 Hz], 86.9 [tm, C(1), $^2J_{C(1)-o-F}$ 25 Hz] (C_6F_5 moiety); 117.5 [t, C(6), $^2J_{C(6)-F(5)}$ 32 Hz], 114.1 [tt, C(1), $^1J_{C(1)-F(1)}$ 346 Hz, $^2J_{C(1)-F(2)}$ 44 Hz], 110.4 [tt, C(2), $^1J_{C(2)-F(2)}$ 271 Hz, $^2J_{C(2)-F(1)}$ 32 Hz], 110.3 [tt, C(3), $^1J_{C(3)-F(3)}$ 272 Hz, $^2J_{C(3)-F(2)}$ 32 Hz], 109.8 [tt, C(4), $^1J_{C(4)-F(4)}$ 271 Hz, $^2J_{C(4)-F(3)}$ 33 Hz], 108.7 [ttq, C(5), $^1J_{C(5)-F(5)}$ 270 Hz, $^2J_{C(5)-F(4)}$ 32 Hz, $^2J_{C(5)-F(6)}$ 26 Hz] (C_6F_{13} moiety). Raman ($-30^\circ C$, FEP-capillary) ($\tilde{\nu}/cm^{-1}$): 1639 (14), 1521 (4), 1413 (11), 1165 (3), 1105 (4), 1012 (6), 988 (2), 883 (2), 845 (9), 809 (6), 751 (20), 644 (4), 618 (3), 588 (20), 528 (2), 496 (23), 442 (13), 354 (9), 254 (29), 202 (20), 140 (11); bands of FEP are omitted.

Salts **1–3** as solids are stable at room temperature for a few days. The solution of **3** in weakly coordinating PFP decomposed above 0 °C (35% conversion at 0 °C within 2 h and 100% conversion after 3 h at 25 °C) to yield equimolar amounts of C₆F₁₄, C₆F₅I and C₆F₁₃BF₂. The solution of **2** in coordinating acetonitrile showed no decomposition at –25 °C within 8 h and a trace of C₆F₅I after 5 h at 0 °C (¹⁹F NMR). However, after 5 h at 22 to 25 °C, the decomposition of **2** to C₆F₁₄, C₆F₅I and BF₃·NCMe exceeded 90%. The decomposition of **3** in MeCN proceeded similarly to give C₆F₁₄, C₆F₅I and C₆F₁₃BF₂·NCMe. In both cases, unknown minor perfluoroalkyl-containing by-products due to reactions with the solvent were detected by ¹⁹F NMR spectroscopy.

§ A cold (–45 °C) solution of C₆F₁₃BF₂ (0.45 mmol) in PFP (2 ml)⁴ was added in portions to the cold (–45 °C) stirred solution of C₆F₅IF₂ (0.22 mmol)⁵ in PFP (1.5 ml). After 1 h at –40 °C the lemon-yellow solution contained [C₆F₁₃(C₆F₅)I]⁺, [(C₆F₅)₂I]⁺, [C₆F₁₃BF₃][–] (55:6:61) besides BF₃ (¹⁹F NMR). The ¹⁹F NMR spectra of a probe (0.4 ml) showed 35% decomposition of **3** after 2 h at 0 °C and 100% decomposition after 3 h at 25 °C under formation of equimolar amounts of C₆F₅I, C₆F₁₄, and C₆F₁₃BF₂. The main solution (2.1 ml) was evaporated to dryness at –20 °C in a vacuum to yield a lemon-yellow solid, [C₆F₁₃(C₆F₅)I][C₆F₁₃BF₃] **3** with an admixture of [(C₆F₅)₂I][C₆F₁₃BF₃] (~18%).

3: ¹⁹F NMR (PFP, –40 °C) δ: –52.8 [m, 2F, F(1)], –80.0 [m, 3F, F(6)], –112.0 [m, 2F, F(2)], –119.9 [m, 2F, F(3)], –121.2 (m, 2F, *o*-F), –121.9 [m, 2F, F(4)], –125.9 [m, 2F, F(5)], –134.4 (t, 1F, *p*-F, ³J_{*p*-F-*m*-F} 20 Hz), –153.4 (m, 2F, *m*-F) ([C₆F₁₃(C₆F₅)I]⁺ moiety); –80.1 [m, 3F, F(6)], –121.8, –122.0, –122.7, –125.4 (8F, 4CF₂), –133.3 [m, 2F, F(1)], –147 (br., 3F, BF₃) ([C₆F₁₃BF₃][–] moiety).

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