

## Two special pathways to perfluoroaryl iodonium salts: the migration of the nucleophilic aryl group in C<sub>6</sub>F<sub>5</sub>IO and the electrophilic arylation of C<sub>6</sub>F<sub>5</sub>I with [C<sub>6</sub>F<sub>5</sub>Xe]<sup>+</sup> salts

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Dedicated to Professor Anastasios Varvoglis on his 65<sup>th</sup> birthday  
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### Abstract

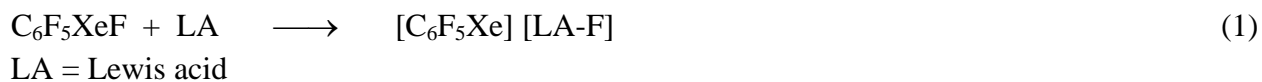
Two theoretically interesting pathways to the perfluorinated diaryliodonium cation [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>I]<sup>+</sup> are described: the electrophilic arylation of C<sub>6</sub>F<sub>5</sub>I by [C<sub>6</sub>F<sub>5</sub>Xe]<sup>+</sup> salts and the nucleophilic migration of a C<sub>6</sub>F<sub>5</sub> group in the iodosyl compound C<sub>6</sub>F<sub>5</sub>IO. The first method allowed also the arylation of C<sub>6</sub>F<sub>5</sub>Br, but failed in the case of C<sub>6</sub>F<sub>5</sub>Cl. Furthermore, the protodeiodination of C<sub>6</sub>F<sub>5</sub>IO and [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>I]<sup>+</sup> in alkaline medium was investigated.

**Keywords:** Pentafluorophenylation, aryl migration, pentafluoroxenonium salts, pentafluorophenyliodosobenzene, bis(pentafluorophenyl)iodonium salts, basic hydrolysis

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### Introduction

Symmetrical diaryliodonium salts [Ar<sub>2</sub>I] X belong to the oldest examples of polyvalent iodine compounds and cover the largest subgroup of the class of iodonium compounds.<sup>1</sup> Only few information has been published on the perfluoroaryl analogues.<sup>2, 3, 4</sup> This is astonishing because the pentafluorophenyl group represents an ideal organo ligand for onium cations which derived from hypervalent molecules. This was most impressively demonstrated in organoxenon chemistry (eq. 1).<sup>5</sup>



Salts such as  $[\text{C}_6\text{F}_5\text{Xe}] [\text{AsF}_6]$  represent thermally stable solids melting (102 °C) without decomposition while the corresponding neutral molecule  $\text{C}_6\text{F}_5\text{XeF}$  is a low temperature species and decomposes at < 20 °C.<sup>6</sup> The pentafluorophenyl group bonded to an onium center of a heavy main group element represents a strong electron-withdrawing ligand without mesomeric interaction and with a high resistance to oxidation. Different to the phenyl group,  $\text{C}_6\text{F}_5$  does not take over remarkable positive charge from the cationic center and is therefore not a favored electrophilic leaving group.

The high electronegativity of the  $\text{C}_6\text{F}_5$  group of 3.27 which is higher than that of chlorine facilitates its good nucleofugality in anionic species.<sup>7</sup> Recently we have published a common synthetic approach to asymmetric iodonium tetrafluoroborates which was proved for a series of pentafluorophenyl(polyfluorophenyl)iodonium tetrafluoroborates. We have investigated their spectroscopic and structural characteristics as well as their thermal stability and have performed ab initio calculations for some representative iodonium cations.<sup>2</sup> The peculiarity of  $[(\text{C}_6\text{F}_5)_2\text{I}]^+_{(\text{g})}$  compared to  $[(\text{C}_6\text{H}_5)_2\text{I}]^+_{(\text{g})}$  is clearly expressed in the Mulliken charges on I of 1.266 versus 0.906 and on the ipso-C atoms of -0.960 versus -0.441. The significant high differences in charge on I and C(1) in  $[(\text{C}_6\text{F}_5)_2\text{I}] [\text{BF}_4]$  are responsible for two relatively strong C-I bonds with two very short I...F cation-anion contacts of 2.84 Å in average compared to 2.94 Å in the non-fluorinated analogue.<sup>8</sup> In this paper we present two specific approaches to  $[(\text{C}_6\text{F}_5)_2\text{I}]^+$  salts which cannot be applied to the corresponding  $[(\text{C}_6\text{H}_5)_2\text{I}]$  salts.

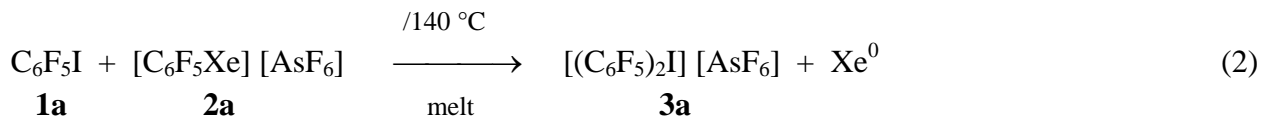
The new procedures to  $[(\text{C}_6\text{F}_5)_2\text{I}]^+$  salts start from  $[\text{C}_6\text{F}_5\text{Xe}]^+$  salts or from the iodosyl compound  $\text{C}_6\text{F}_5\text{IO}$ . The latter was first synthesized by Schmeißer in 1967.<sup>9</sup> In 1980 investigations in super acidic media were reported<sup>10</sup> and since 1985  $\text{C}_6\text{F}_5\text{IO}$  was introduced in numerous metal-based epoxidation/oxygenation reactions.<sup>11</sup> Unfortunately the thermal stability and the structure of **4a** discussed in literature is controversial. Thus the decomposition temperatures ranging from 88 to 210 °C.<sup>9, 12</sup> To our knowledge nothing is known about the products of thermal decomposition of  $\text{C}_6\text{F}_5\text{IO}$ . For 2,4,6- $\text{C}_6\text{H}_2\text{Cl}_3\text{IO}$  with a less electron-poor aryl group Willgerodt investigated its thermolysis upon steam distillation and reported 2,4,6- $\text{C}_6\text{H}_2\text{Cl}_3\text{I}$ ,  $\text{HIO}_3$ , and  $\text{CO}_2$  as decomposition products, no formation of an iodonium compound was mentioned.<sup>13</sup>

## Results and Discussion

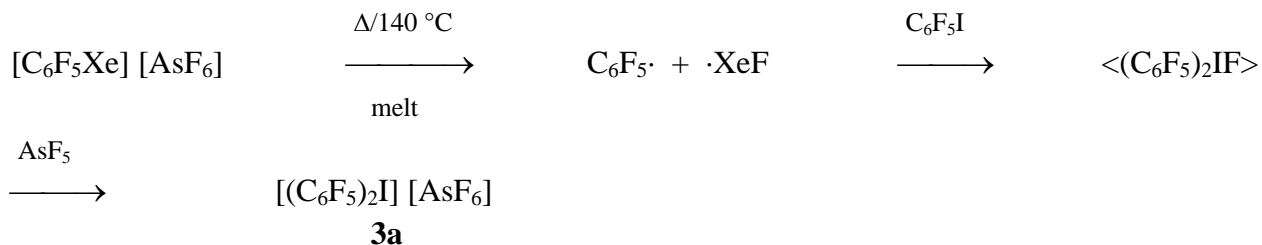
### The electrophilic pentafluorophenylation of $\text{C}_6\text{F}_5\text{I}$

The aryl group in  $\text{C}_6\text{F}_5\text{I}$  (**1a**), different to  $\text{C}_6\text{H}_5\text{I}$  (**1b**), resists all attempts of electrophilic substitution because  $\text{F}^+$  does not represent a realistic leaving group by thermodynamic arguments. Despite the higher positive Mulliken charge on iodine in **1a** (0.368) compared to **1b** (0.164),<sup>2</sup> **1a** reacted with suitable formal sources of  $[\text{C}_6\text{F}_5]^+$  such as  $[\text{C}_6\text{F}_5\text{Xe}]^+$  salts. But the reactivity of the  $[\text{C}_6\text{F}_5\text{Xe}]^+$  cation (**2**) depended strongly on the reaction conditions. **1a** did neither react with  $[\text{C}_6\text{F}_5\text{Xe}] [\text{AsF}_6]$  (**2a**) in MeCN solution at 20 °C within 70 hours nor with

[C<sub>6</sub>F<sub>5</sub>Xe] [BF<sub>4</sub>] in boiling MeCN within 4 hours (homogenous reactions) nor with **2a** in CH<sub>2</sub>Cl<sub>2</sub> suspension under pressure at 80 °C within 4 hours. However the pentafluorophenylation was successful in the high viscous melt of **2a** and a 10-fold excess of **1a** at 140 °C (eq. 2).



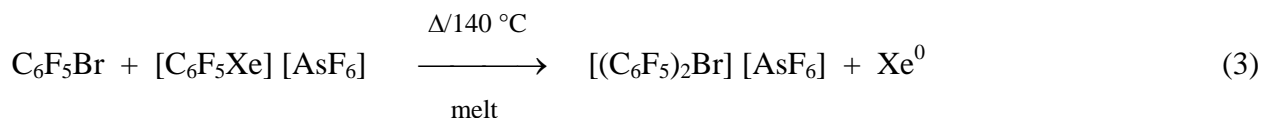
**2a** was consumed within 1 hour and pure **3a** was isolated in 20 % yield. The different reactivities in the above mentioned systems of **1a/2** reflect the coordination moiety at Xe. In **2a** no naked cation **2** is present. In MeCN solution the hard N-atom is coordinated<sup>14</sup> and in crystalline **2a** strong cation-anion contacts were found despite of the weak coordinating character of the anion [AsF<sub>6</sub>]<sup>-</sup>.<sup>15</sup> In the melt of **2a** slow decomposition proceeded above 125 °C with the formation of equimolar quantities of C<sub>6</sub>F<sub>6</sub> and AsF<sub>5</sub>. The products can be best explained by the intermediate formation of C<sub>6</sub>F<sub>5</sub>XeF which forms C<sub>6</sub>F<sub>6</sub> and Xe in a subsequent step. There is strong evidence that the decomposition of C<sub>6</sub>F<sub>5</sub>XeF proceeds via the homolytic cleavage of the C-Xe bond.<sup>3</sup> Formal addition of the C<sub>6</sub>F<sub>5</sub> and F radical to C<sub>6</sub>F<sub>5</sub>I followed by the abstraction of the fluoride ion by the Lewis acid which is present, resulted in the iodonium salt **3a** (Scheme 1).



**Scheme 1.** The pentafluorophenylation of pentafluoriodobenzene (**1a**).

At first glance the negative result in MeCN solution contradicts to an earlier published result that [C<sub>6</sub>F<sub>5</sub>Xe] [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>BF] was able to arylate C<sub>6</sub>F<sub>5</sub>I in MeCN at ambient temperature in the presence of an excess of (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B.<sup>4</sup> [C<sub>6</sub>F<sub>5</sub>Xe] [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>BF] is not stable at room temperature and contains two nucleophilic sites: the ipso-C-atoms and the F-atom bonded to boron. Thus C<sub>6</sub>F<sub>5</sub>XeF may be the decisive intermediate which can add to C<sub>6</sub>F<sub>5</sub>I. Finally the Lewis acid (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B which was present in excess may have allowed the transformation to the corresponding iodonium salt [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>I] [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>BF].

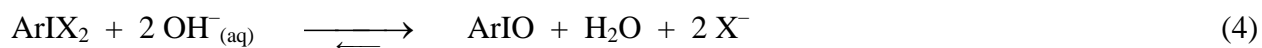
The method of adding formally the [C<sub>6</sub>F<sub>5</sub>]<sup>+</sup> cation to a n-base could be successfully extended to C<sub>6</sub>F<sub>5</sub>Br. For C<sub>6</sub>F<sub>5</sub>Cl we were not able to find positive reaction conditions.



An excess of  $\text{C}_6\text{F}_5\text{Br}$  was reacted in the melt of **2a** under the same conditions as reported for  $\text{C}_6\text{F}_5\text{I}$ . In contrast to the completed reaction of **1a** in the case of  $\text{C}_6\text{F}_5\text{Br}$  ca. 11 % of initial **2a** beside only 6 % of the final product  $[(\text{C}_6\text{F}_5)_2\text{Br}] [\text{AsF}_6]$  were still found after 1 h. The lower reactivity of the bromo compound with respect to the corresponding iodo analogue and the missing reactivity of  $\text{C}_6\text{F}_5\text{Cl}$  follows the IP values of  $\text{C}_6\text{F}_5\text{Hal}$ : I = 9.5 eV, Br = 9.67 eV, and Cl = 9.7 eV.<sup>16</sup> Whereas the charge at Hal in  $\text{C}_6\text{F}_5\text{Hal}$  has no direct influence on the reactivity as proven by the natural charges (NBO, RHF, LAN2DZ basis set) in the series of  $\text{C}_6\text{F}_5\text{Hal}$  compounds with I = 0.321, Br = 0.169, Cl = 0.023, and F = -0.367.

**The formation of  $[(\text{C}_6\text{F}_5)_2\text{I}] [\text{IO}_3]$  by migration of the nucleophilic aryl group in  $\text{C}_6\text{F}_5\text{IO}$**

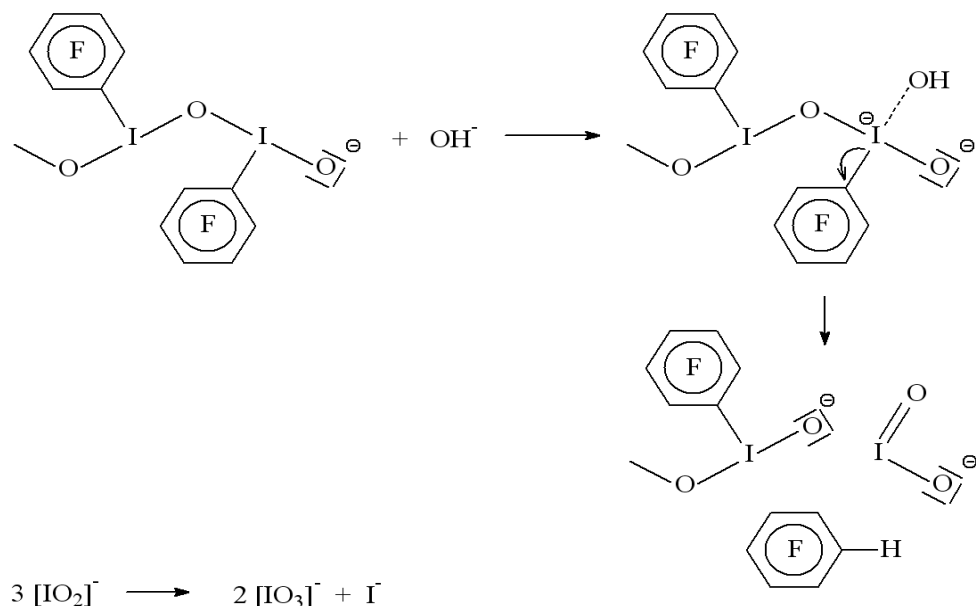
$\text{C}_6\text{F}_5\text{IO}$  (**4a**) like non-fluorinated  $\text{C}_6\text{H}_5\text{IO}$  (**4b**) is a polymeric, non-crystalline solid which is obtained by hydrolysis from mixed anhydrides  $\text{ArIX}_2$ :



X = OAc, Hal, etc.

In analogy to the precursor  $\text{ArIX}_2$  we propose a T-shape arrangement at iodine(III) in **4a** with a 2c-2e C-I bond and a linear 3c-4e O-I-O triad with a high positive partial charge on iodine and distinct negative partial charges on both bridging oxygen atoms.<sup>17</sup>

**4a** was prepared from the corresponding pentafluorophenyl iodine(III)bis(trifluoroacetate) or -difluoride using saturated  $\text{NaHCO}_3_{(\text{aq})}$  solutions of  $\text{pH} \leq 10$ . To achieve full hydrolysis magnetic stirring was necessary over a very long reaction time of > 1 d. Intensive stirring (Ultra-Turrax) at 0 °C shortened the time of hydrolysis to less than 1 h. A more alkaline medium like a 1 m  $\text{NaOH}_{(\text{aq})}$  must be avoided to prevent the complete C-I bond cleavage. The nucleophilic attack of  $\text{OH}^-$  on the I-atom initiated a shift of negative charge to the electronegative  $\text{C}_6\text{F}_5$  group which leaves the intermediate anion and adds a proton forming  $\text{C}_6\text{F}_5\text{H}$ . The unstable  $[\text{IO}_2]^-$  anion as co-product disproportionates to  $\text{I}^-$  and  $[\text{IO}_3]^-$  (Scheme 2).

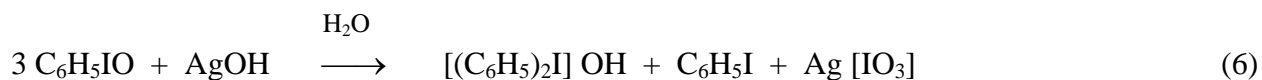


**Scheme 2.** The protodeiodination of polymeric  $\text{C}_6\text{F}_5\text{IO}$ .

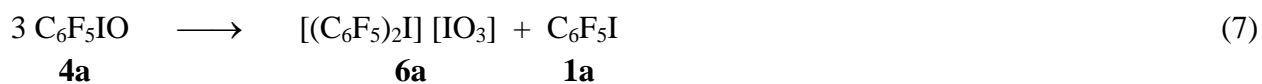
The most remarkable property of the non-fluorinated iodosylbenzene **4b** is its ability to disproportionate under controlled thermal conditions (steam distillation) yielding iodylbenzene  $\text{C}_6\text{H}_5\text{IO}_2$  and iodobenzene (eq. 5).



Since the early work of Meyer<sup>18</sup> a further redox reaction of **4b** under basic conditions is known in aqueous medium (eq. 6).

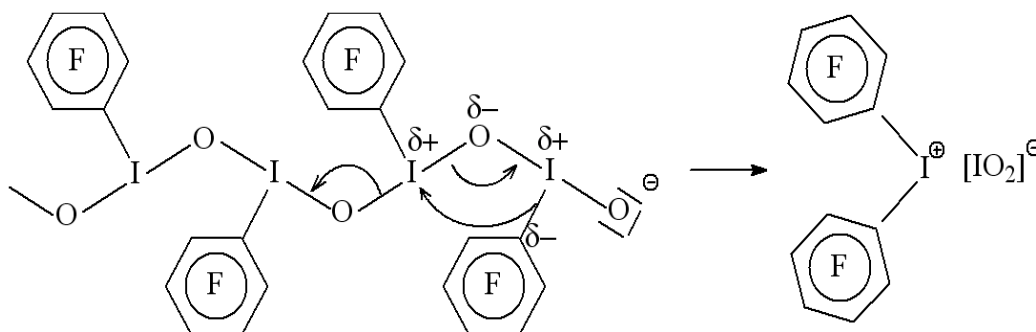


This reaction has been explained by Masson<sup>19</sup> and Johnson<sup>20</sup> based on monomeric **4b** by a sequence of dipolar additions or formal redox reactions. In this work we will show that the aimed thermolysis of **4a** in the absence of a basic reagent in different media, aprotic included, ends with similar products according to eq. 6 and is best approximated by eq. 7:

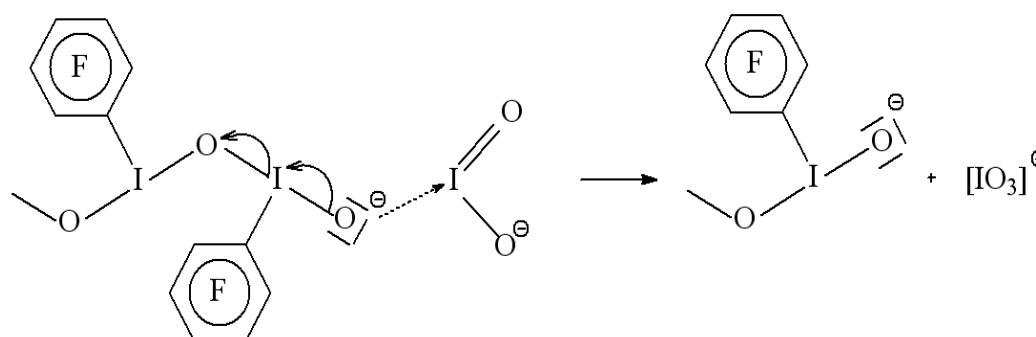


During its thermal decomposition  $C_6F_5IO$  tends to explode.<sup>12</sup> Therefore we decided to investigate this reaction only in gram scale and in the presence of an inert liquid media such as  $C_6F_5I$ ,  $C_6F_5Cl$ ,  $CCl_4$ ,  $C_6H_6$ , or  $H_2O$ , which allow to dissipate the heat of decomposition. We have found optimal conditions for the decomposition at a bath temperature of 100 °C and performed the thermolysis in a rotating flask (rotary evaporator) which contained glass spheres of 4 mm diameter. This precaution prohibited the coagulation of larger amounts of solid **4a** and minimized the formation of hot spots. The yield of **6a** after isolation and purification was always only in the range of 40 to 60 %, whereas the yield of  $C_6F_5I$  was  $\geq 120$  %, both yields were based on eq. 7. In one case we proved the gas phase during the decomposition with an Orsat analyzer for  $CO_2$  and  $O_2$ . The yield of both gaseous products was only 5 and 3 %, respectively. We explain the formation of the iodonium cation  $[(C_6F_5)_2I]^+$  by the migration of the nucleophilic  $C_6F_5$  group at the terminal iodine in the polymeric chain to a positive iodine neighbor center. This process is initiated by the deprotonation of the terminal I-OH group. It should be emphasized that polymeric **4a** and **4b** differ in their acidity of terminal OH groups. The negatively charged oxygen at the end of the I-O chain activates the nucleofugality of the  $C_6F_5$  neighbor group and initiates the migration. Scheme 3 explains in the first step the formation of  $[(C_6F_5)_2I] [IO_2]$ . The redox unstable  $[IO_2]^-$  anion interacts as Lewis acid with the terminal oxygen base of **4a** in the direct moiety. In this redox reaction equivalent quantities of **1a** and  $[IO_3]^-$  were obtained.

When the thermolysis was performed in the protic medium water no  $C_6F_5H$  was formed indicating that the migration of the nucleophilic  $C_6F_5$  group was favored over the addition of a proton. In the aqueous medium no iodine from a disproportionation of  $[IO_2]^-$  was observed which means that no acid was formed. The conversion of  $[IO_2]^-$  to  $[IO_3]^-$  needs a strong oxidizer, presumably **4a**, see step 2, Scheme 3. The thermolysis of **4a** in  $C_6H_6$  in the presence of Ag  $[ClO_4]$  with the weak nucleophilic anion  $[ClO_4]^-$  and under conditions where the  $[IO_3]^-$  anion was precipitated as Ag  $[IO_3]$  did not change the reaction path. The iodonium cation was finally isolated as  $[(C_6F_5)_2I] [ClO_4]$  (**8a**).



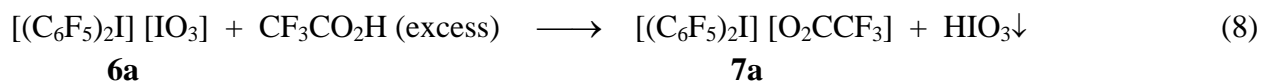
The first step: the migration of the nucleophilic pentafluorophenyl group.



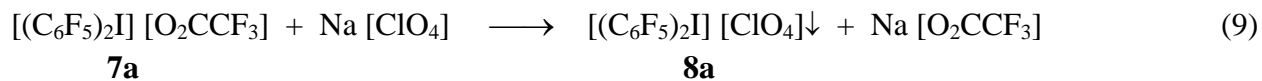
The following redox step: the deoxygenation of  $C_6F_5IO$  by  $[IO_2]^-$ .

**Scheme 3.** The thermolysis of polymeric  $C_6F_5IO$ .

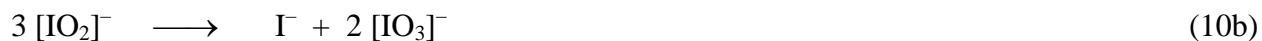
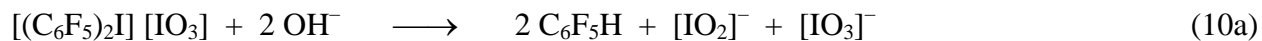
Additionally to the spectroscopic and analytical methods we proved the constitution of **6a** by two metathesis reactions. In the first step **6a** was reacted with neat  $CF_3CO_2H$  and converted to  $[(C_6F_5)_2I][O_2CCF_3]$  (**7a**) and  $HIO_3$  (eq. 8).



The cation anion ratio of **7a** was unambiguously characterized by the integrals in the  $^{19}F$  NMR spectrum.  $HIO_3$  was identified by its molecular weight, determined by iodometry. The solubility of **7a** in aqueous acetone allowed a further metathesis e.g. the convenient substitution of the  $[CF_3CO_2]^-$  anion by the  $[ClO_4]^-$  anion (eq. 9).



When **6a** was heated in a 1 M NaOH suspension protodeiodination of the cation proceeded and C<sub>6</sub>F<sub>5</sub>H was formed beside [IO<sub>2</sub>]<sup>-</sup> which disproportionate to give I<sup>-</sup> and [IO<sub>3</sub>]<sup>-</sup>, eq. 10, compare Scheme 2.



The different literature statements about the thermal stability of **4a** can now be explained. Freshly prepared **4a** from C<sub>6</sub>F<sub>5</sub>IX<sub>2</sub> without residual amounts of terminal groups X in the polymer decomposes at ca. 89 °C. **4a** stored e.g. at 30 °C over a longer period of time (ca. 1 m) undergoes a transformation to **6a** and **1a** comparable to the fast process described in eq. 7. Thus the reported decomposition of **4a** at 210 °C<sup>12</sup> can be attributed to **6a**.

## Experimental Section

**General Procedures.** C<sub>6</sub>F<sub>5</sub>I(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> was prepared from **1a**, 100 % HNO<sub>3</sub> and (CF<sub>3</sub>CO)<sub>2</sub>O and purified by recrystallization from CCl<sub>4</sub> followed by sublimation (80 °C/10<sup>-3</sup> hPa); mp 117 – 8 °C.<sup>9</sup> C<sub>6</sub>F<sub>5</sub>IF<sub>2</sub>,<sup>17</sup> [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>],<sup>15</sup> and [C<sub>6</sub>F<sub>5</sub>Xe][BF<sub>4</sub>]<sup>21</sup> were obtained by literature methods.

**Pentafluorophenylation of C<sub>6</sub>F<sub>5</sub>I (1a) using the melt of [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] (2a).** **1a** (392 mg, 1.33 mmol) was added to solid **2a** (65 mg, 0.13 mmol) in a FEP-trap (D<sub>i</sub> = 3.5 mm). The mixture was heated in the closed trap at 140 °C under a dry atmosphere of Ar for 1 h. After cooling to 20 °C and extraction with CH<sub>2</sub>Cl<sub>2</sub> (4 times 0.3 ml) the white solid was dried in high vacuum and dissolved in CD<sub>3</sub>CN. [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>I][AsF<sub>6</sub>] (**3a**) was obtained in 20 % yield (<sup>19</sup>F NMR, quantitative standard). The CH<sub>2</sub>Cl<sub>2</sub> extracts contained C<sub>6</sub>F<sub>5</sub>I (excess of starting material, <sup>19</sup>F NMR: -120.1, -153.1, -160.4 ppm) and C<sub>6</sub>F<sub>6</sub> (minor component, <sup>19</sup>F NMR: -162.9 ppm). **3a** <sup>19</sup>F NMR (CD<sub>3</sub>CN): δ/ppm -120.3 *o*-F, -140.9 *m*-F, -155.2 *m*-F, -64.6 AsF, 1:1:1:1 q, <sup>1</sup>J<sub>F,As</sub> = 931 Hz.

**Attempted reaction of C<sub>6</sub>F<sub>5</sub>I (1a) with [C<sub>6</sub>F<sub>5</sub>Xe]<sup>+</sup> salts (2) in MeCN solution.** **1a** (392 mg, 1.33 mmol) was added to a MeCN (0.5 ml) solution of [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] **2a** (65 mg, 0.13 mmol) in a FEP-trap (D<sub>i</sub> = 3.5 mm). Neither a consumption of [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] nor formation of [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>I][AsF<sub>6</sub>] was detected (<sup>19</sup>F NMR) over 3d at 20 °C. [C<sub>6</sub>F<sub>5</sub>Xe][BF<sub>4</sub>] also did not react with **1a** when heated at 80 °C for 4 h.

**Attempted reaction of C<sub>6</sub>F<sub>5</sub>I (1a) with [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] (2a) in CH<sub>2</sub>Cl<sub>2</sub> suspension.** **1a** (392 mg, 1.33 mmol) was added to the CH<sub>2</sub>Cl<sub>2</sub> (0.5 ml) suspension of [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] **2a** (65 mg, 0.13 mmol) in a FEP-trap (D<sub>i</sub> = 3.5 mm). The closed trap was heated under pressure at 80 °C for 4 h. The mother liquor containing only C<sub>6</sub>F<sub>5</sub>I was removed, the solid residue was washed with CH<sub>2</sub>Cl<sub>2</sub> (4 times 0.3 ml), dried, dissolved in CD<sub>3</sub>CN and identified as [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] (<sup>19</sup>F NMR).



**Pentafluorophenylation of C<sub>6</sub>F<sub>5</sub>Br using the melt of [C<sub>6</sub>F<sub>5</sub>Xe] [AsF<sub>6</sub>] (2a).** C<sub>6</sub>F<sub>5</sub>Br (213 mg, 0.86 mmol) was added to solid [C<sub>6</sub>F<sub>5</sub>Xe] [AsF<sub>6</sub>] (42 mg, 0.09 mmol) in a FEP-trap (D<sub>i</sub> = 3.5 mm) and heated at 140 °C for 1 h. After cooling to 20 °C and extraction with CH<sub>2</sub>Cl<sub>2</sub> (4 times 0.3 ml) the remaining white solid was dried in high vacuum and dissolved in CD<sub>3</sub>CN. Beside the product [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Br] [AsF<sub>6</sub>] (<sup>19</sup>F NMR: -128.8 *o*-F, -138.7 *p*-F, -154.2 *m*-F, -64.6 ppm AsF, 1:1:1:1 q, <sup>1</sup>J<sub>F,As</sub> = 930 Hz) the starting material [C<sub>6</sub>F<sub>5</sub>Xe] [AsF<sub>6</sub>] was still present in amounts of 6 and 11 %, respectively. The CH<sub>2</sub>Cl<sub>2</sub> extracts contained C<sub>6</sub>F<sub>5</sub>Br (excess of starting material, <sup>19</sup>F NMR: -133.2 *o*-F, -154.9 *p*-F, -161.1 ppm *m*-F) and C<sub>6</sub>F<sub>6</sub> (83 %, <sup>19</sup>F NMR: -162.9 ppm).

**Hydrolysis of C<sub>6</sub>F<sub>5</sub>I(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> in the presence of increasing amounts of base.** C<sub>6</sub>F<sub>5</sub>I(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> (2.0 g, 3.9 mmol) suspended in 100 ml water was magnetically stirred in the presence of 0 (a), 1 (b), 2 (c), and 4 (d) equivalents of NaHCO<sub>3</sub> for 15 h, respectively. The resulting solids were separated, washed with water (3 times, 50 ml) and dried (20 °C/10<sup>-3</sup> hPa) for 6 h. The pale yellow products differ in their temperature of decomposition, in their IR spectra (presence of CF<sub>3</sub>CO<sub>2</sub> groups) and their molecular weight determined by iodometry (based on C<sub>6</sub>F<sub>5</sub>I<sup>II</sup> + 2 I<sup>-</sup> → C<sub>6</sub>F<sub>5</sub>I + I<sub>2</sub>).

(a) dec. 187 °C, IR: CF<sub>3</sub>CO<sub>2</sub> present, (b) dec. 176 °C, IR: CF<sub>3</sub>CO<sub>2</sub> present, M(iodometric) 396.7 g mol<sup>-1</sup>, (c) dec. 218 °C, IR: CF<sub>3</sub>CO<sub>2</sub> present, (d) dec. 81 °C, IR: no CF<sub>3</sub>CO<sub>2</sub> found, M(iodometric) 323.4 (calc. 309.96) g mol<sup>-1</sup>.

**Formation of 4a by an optimized fast hydrolysis.** Finely ground C<sub>6</sub>F<sub>5</sub>I(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> (2.07 g, 3.98 mmol) was suspended in 100 ml of saturated NaHCO<sub>3(aq)</sub> at 0 °C. The cooled (ice bath) suspension was stirred with an Ultra-Turrax (Janke & Kunkel) stirrer T 25, 12000 cm<sup>-1</sup> for 15 min.. After filtration the solid was stirred again with 100 ml water for 10 min. (the mother liquor was neutral). The solid product was separated and washed with water (3 times, 50 ml) and dried (20 °C/10<sup>-3</sup> hPa) for 10 h. The yield of **4a** was 1.0 g (81 %). The pale yellow solid had a molecular weight determined by iodometry of 314.3 (calc. 309.96) g mol<sup>-1</sup> and decomposed at 89 °C. **4a** was also prepared from C<sub>6</sub>F<sub>5</sub>IF<sub>2</sub> using the same procedure. No polar solvent was found for NMR measurements of **4a**. In pure MeCN decomposition to C<sub>6</sub>F<sub>5</sub>I proceeded during dissolution, in acidic solvents solvolysis. **4a**. IR ( $\bar{\nu}$ , cm<sup>-1</sup>) 1632 w, 1512 m, 1480 s, 1400 m, 1372 w, 1340 w, 1290 m, 1158 w, 1147 sh, 1090 s, 1005 m, 978 s, 808 s, 720 w, 710 sh, 589 w, 450 s, 380 sh, 368 m, 353 sh, 310 m. Ra ( $\bar{\nu}$ , 500 - 150 cm<sup>-1</sup>) 498 m, 450 vs, 393 w, 364 s, 355 sh, 227 m, 195 s (C-I), 175 sh.

### Thermolysis of C<sub>6</sub>F<sub>5</sub>IO (4a) and formation of [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>I] [IO<sub>3</sub>] (6a)

**a) Thermolysis of 4a in C<sub>6</sub>F<sub>5</sub>I using a rotary evaporator.** The rotating flask of the evaporator was charged with glass spheres (65 g), freshly prepared **4a** (8.0 g, 26 mmol) and **1a** (15 ml) under an atmosphere of dry Ar. Within 30 min. the mixture was heated to 100 °C under rotation and **explosion protection**. After ca. 3 hours the suspension changed to a yellow solution before precipitation started slowly. After 6 h reaction time the suspension was cooled to 20 °C. The white solid was separated, washed with CCl<sub>4</sub> and dried in high vacuum. Impurities of iodonium salts with the anions [SiF<sub>6</sub>]<sup>-</sup> (<sup>19</sup>F NMR: -125.3) and [BF<sub>4</sub>]<sup>-</sup> (<sup>19</sup>F NMR: -150.0, traces) - both

from etching of the glass - were removed by extraction using MeCN. The yield of **6a** was 2.5 g, 46 %; dec. 212 °C, M(iodometric) 631.7 (calc. 635.92)  $\text{g mol}^{-1}$ . **6a**: practically insoluble in MeCN, acetone and MeOH;  $^{19}\text{F}$  NMR ( $\text{D}_2\text{O}$ )  $\delta/\text{ppm}$ : -124.0 *o*-F, -143.7 *p*-F, -157.6 *m*-F; IR ( $\bar{\nu}$ ,  $\text{cm}^{-1}$ ) 1632 w, 1512 sh, 1498 s, 1397 m, 1287 m, 1155 w, 1088 s, 1004 m, 980 s, 823 m (I-O, E), 802 sh, 795 sh, 778 sh (I-O,  $\text{A}_1$ ), 762 sh, 742 s, 730 sh, 722 sh, 623 w, 587 vw, 490 vs, 377 m (I-O,  $\text{A}_1$ ), 340 w (I-O, E), 270 w. Ra ( $\bar{\nu}$ , 850 - 150  $\text{cm}^{-1}$ ) 823 w (I-O, E), 779 s (I-O,  $\text{A}_1$ ), 769 w, 738 s, 723 w, 493 s, 445 w, 389 m (I-O,  $\text{A}_1$ ), 351 m (I-O, E), 277 m, 210 m, 189 s (C-I).

**b) Thermolysis of 4a in water using a rotary evaporator.** Using the above procedure **4a** (4.2 g, 14 mmol) was heated in water (100 ml) at 100 °C for 6 h. **6a** (1.7 g, 60 %) was isolated as solid and **1a** (1.6 g, 120 %) by extraction of the aqueous phase with  $\text{CCl}_4$ . A comparable treatment in water at 50 to 60 °C for 5 h showed no conversion of **4a** to **6a**.

**c) Thermolysis of 4a in 1a and monitoring of the gas phase.** A flask with **4a** (4.0 g, 13 mmol) and **1a** (10.8 g) equipped with a condenser which was connected by a three-way-stopcock to a Orsat gas analyzer. After evaporation of the reaction system at -50 °C dry Ar was introduced until normal pressure was achieved. The reaction mixture was then warmed to 100 °C monitoring the pressure. After 6 h the increase of pressure could be neglected. The gas phase was analyzed (ca. 0.7 mmol  $\text{CO}_2$  and 0.4 mmol  $\text{O}_2$ ). **6a** (1.8 g, 64 % yield) was isolated from the suspension.

**d) Thermolysis of 4a in  $\text{C}_6\text{H}_6$  in the presence of Ag  $[\text{ClO}_4]$ .** In a further modification a stirred suspension of **4a** (1.0 g, 3.2 mmol) and Ag  $[\text{ClO}_4]$  (0.5 g, 2.4 mmol) in dry benzene (5 ml) was refluxed for 2 h. The solid material was separated, washed with  $\text{C}_6\text{H}_6$  (0.5 ml), and dried. The white solid was extracted with hot water (60 °C, 3 times 25 ml). The residue consisted of Ag  $[\text{IO}_3]$  (IR, iodometry). The solvent was removed from the extract and the remaining solid was dried in vacuum. It consisted only of  $[(\text{C}_6\text{F}_5)_2\text{I}] [\text{ClO}_4]$ , characterized by IR, Ra and mp (dec. 263 °C) in comparison with the metathesis product from the reaction of  $[(\text{C}_6\text{F}_5)_2\text{I}] [\text{O}_2\text{CCF}_3]$  and Na  $[\text{ClO}_4]$  in acetone/water (see later).

**e) The thermal treatment of  $\text{C}_6\text{F}_5\text{IO}$  (**4a**) in alkaline aqueous medium.** In a flask with condenser **4a** (3.0 g, 9.7 mmol) was heated in 30 ml of 1 M  $\text{NaOH}_{(\text{aq})}$  at 100 °C for 3 h. After 1h a product started to reflux and all solid disappeared. The volatile resultant was distilled off and identified as  $\text{C}_6\text{F}_5\text{H}$  by  $^{19}\text{F}$  NMR and IR. The  $^{19}\text{F}$  NMR of the  $\text{CCl}_4$  extract of the aqueous phase exhibits no further  $\text{C}_6\text{F}_5$  compound. In the aqueous phase the molar ratio of  $\text{I}^-$  to  $[\text{IO}_3]^-$  was determined by iodometry to 1 to 2.1.

**f) The long term storage and decomposition of neat  $\text{C}_6\text{F}_5\text{IO}$  (**4a**).** A sample of **4a** (491 mg) was stored at ca. 30 °C for 1 month. Afterwards all volatile products were pumped off ( $10^{-3}$  hPa). The weight of the volatile part was 164 (calc. 155 mg) and of the residue 327 (calc. 336 mg). The calculation was based on eq. 7. The volatile product was identified as **1a** by  $^{19}\text{F}$  NMR and the solid residue as **6a** by IR.

**The decomposition of [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>I] [IO<sub>3</sub>] (6a) in 1 M aqueous NaOH.** 1 M NaOH<sub>(aq)</sub> (20 ml) was added to **6a** (1.0 g, 1.6 mmol) in a flask equipped with condenser and magnetic stirrer. When warmed to 80 °C the suspension disappeared and refluxing started. Volatile C<sub>6</sub>F<sub>5</sub>H was separated by distillation and identified by <sup>19</sup>F NMR. Extraction of the aqueous phase with CCl<sub>4</sub> showed no further C<sub>6</sub>F<sub>5</sub> compound by <sup>19</sup>F NMR. Iodometric analysis of the aqueous phase revealed a molar ratio I<sup>-</sup> to [IO<sub>3</sub>]<sup>-</sup> of 1 : 2.8.

**The metathesis of [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>I] [IO<sub>3</sub>] (6a): formation of [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>I] [O<sub>2</sub>CCF<sub>3</sub>] (7a).** **6a** (2.0 g, 3.1 mmol) was treated with CF<sub>3</sub>CO<sub>2</sub>H (3 times, 20 ml) at 40 °C under intensive stirring. The iodonium salt dissolved and a white solid (identified as HIO<sub>3</sub> by iodometric analysis) precipitated. The mother liquors were separated and added to 200 ml H<sub>2</sub>O. **7a** precipitated, was separated, dried, and recrystallized from CF<sub>3</sub>CO<sub>2</sub>H (5 ml) and H<sub>2</sub>O (150 ml). After working up **7a** (1.3 g, 81 %) was isolated. **7a** decomposed at 226 °C. **7a**: <sup>19</sup>F NMR (MeCN) δ/ppm: -122.7 *o*-F, -145.1 *p*-F, -156.9 *m*-F, -74.1 CF<sub>3</sub>; IR ( $\bar{\nu}$ , cm<sup>-1</sup>): 1655 vs (CO<sub>2(as)</sub>), 1635 sh, 1512 sh, 1507 vs, 1435 m, 1417 m, 1405 s, 1375 w, 1399 w, 1255 sh, 1210 sh, 1200 s, 1155 s, 1090 vs, 1083 sh, 1054 sh, 1020 m, 1005 sh, 983 vs, 845 s, 810 s, 900 s, 730 s, 722 sh, 630 w, 623 vw, 608 vw, 452 w, 412 w, 390 w, 363 w, 315 sh; Ra ( $\bar{\nu}$ , cm<sup>-1</sup>): 1642 sh, 1635 w, 1435 m, 1285 w, 1193 w, 1090 m, 850 m, 810 w, 779 w, 623 w, 585 s, 495 vs, 440 m, 390 m, 352 m, 206 s, 194 vs (C-I).

**The metathesis of [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>I] [O<sub>2</sub>CCF<sub>3</sub>] (7a): formation of [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>I] [ClO<sub>4</sub>] (8a).** **7a** (300 mg, 0.6 mmol) was dissolved in acetone/H<sub>2</sub>O (4 : 1, 50 ml) and added drop wise to the stirred solution of Na [ClO<sub>4</sub>] (10.0 g, 81.7 mmol) in water (20 ml). Acetone was removed from the solution using a water jet pump vacuum and the resulting white precipitate was separated, washed with water (3 times 0.5 ml) and dried in high vacuum. **8a** (200 mg, 62 %) decomposed at 265 °C. **8a**: <sup>19</sup>F NMR (MeCN): δ/ppm -120.4 *o*-F, -141.5 *p*-F, -155.5 *m*-F; IR ( $\bar{\nu}$ , cm<sup>-1</sup>): 1635 w, 1512 sh, 1507 vs, 1425 sh, 1405 s, 1375 w, 1300 w, 1160 sh, 1140 s, 1110 vs (Cl-O, F<sub>2</sub>), 1054 vs, 1015 m, 1000 sh, 983 vs, 925 w, 810 s, 800 s, 722 m, 630 s, 623 s (Cl-O, F<sub>2</sub>), 588 w, 390 m, 363 sh, 352 sh, 315 sh; Ra ( $\bar{\nu}$ , cm<sup>-1</sup>): 1635 w, 1090 w, 932 sh, 920 s (Cl-O, A<sub>1</sub>), 792 w, 623 w (Cl-O, F<sub>2</sub>), 585 m, 495 vs, 463 w (Cl-O, E), 435 m, 398 m, 352 m, 283 w, 200 vs (C-I), 190 m.

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