Syntheses, structures, and stabilities of aliphatic and aromatic fluorous iodine(I) and iodine(III) compounds: the role of iodine Lewis basicity

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Abstract

The title molecules are sought in connection with various synthetic applications. The aliphatic fluorous alcohols RfnCH2OH (Rfn = CF3(CF2)n–1; n = 11, 13, 15) are converted to the triflates RfnCH2OTf (Tf2O, pyridine; 22–61%) and then to RfnCH2I (NaI, acetone; 58–69%). Subsequent reactions with NaOCl/HCl give iodine(III) dichlorides RfnCH2ICl2 (n = 11, 13; 33–81%), which slowly evolve Cl2. The ethereal fluorous alcohols CF3CF2CF2O(CF(CF3)CF2O)xCF(CF3)CH2OH (x = 2–5) are similarly converted to triflates and then to iodides, but efforts to generate the corresponding dichlorides fail. Substrates lacking a methylene group, RfnI, are also inert, but additions of TMSCl to bis(trifluoroacetates) RfnI(OCOCF3)2 appear to generate RfnICl2, which rapidly evolve Cl2. The aromatic fluorous iodides 1,3-RfnC6H4I, 1,4-RfnC6H4I, and 1,3-Rf10C6H4I are prepared from the corresponding diiodides, copper, and RfnI (110–130 °C, 50–60%), and afford quite stable RfnC6H4ICl2 species upon reaction with NaOCl/HCl (80–89%). Iodinations of 1,3-(Rf6)2C6H4 and 1,3-(Rf8CH2CH2)2C6H4 (NIS or I2/H5IO6) give 1,3,5-(Rf6)2C6H3I and 1,2,4-(Rf8CH2CH2)2C6H3I (77–93%). The former, the crystal structure of which is determined, reacts with Cl2 to give a 75:25 ArICl2/ArI mixture, but partial Cl2 evolution occurs upon work-up. The latter gives the easily isolated dichloride 1,2,4-(Rf8CH2CH2)2C6H3ICl2 (89%). The relative thermodynamic ease of dichlorination of these and other iodine(I) compounds is probed by DFT calculations.
Introduction

A number of fluorous alkyl iodides, usually of the formula R<sub>f</sub><sub>n</sub>CH<sub>2</sub>CH<sub>2</sub>I or R<sub>f</sub><sub>n</sub>I (R<sub>f</sub><sub>n</sub> = CF<sub>3</sub>(CF<sub>2</sub>)<sub>n-1</sub>), are commercially available and have seen abundant use as building blocks in fluorous chemistry [1-3]. Fluorous aryl iodides, such as R<sub>f</sub><sub>n</sub>C<sub>6</sub>H<sub>4</sub>I or R<sub>f</sub><sub>n</sub>(CH<sub>2</sub>)<sub>m</sub>C<sub>6</sub>H<sub>4</sub>I species, are also often employed as intermediates (typically m = 2, 3 and n ≥ 6 [1-3]), but only a few have been commercialized [4]. Many research groups have described the syntheses of other types of fluorous alkyl [5-8] and aryl [9-12] iodides [13-17]. The former are ubiquitous by virtue of the large number of perfluoroalkyl iodides R<sub>f</sub><sub>n</sub>I that have been shown to undergo free radical additions to alkenes [7,8].

In previous papers, we have reported convenient preparations of a variety of fluorous alkyl iodides [13-15], aryl iodides [16,17], and hypervalent iodine(III) derivatives [16-19]. The latter have included aliphatic iodine(III) bis(trifluoroacetates) [18,19] and dichlorides [17], and aromatic iodine(III) bis(acetates) [16] and dichlorides [17]. The bis(carboxylates) have been employed as recyclable reagents for oxidations of organic substrates [16,18,19], and some of the dichlorides are depicted in Scheme 1. Others have described additional fluorous iodine(III) species [11,20-22].

Recently, our attention has been directed at two potential applications of iodine containing fluorous compounds. One involves new approaches to phosphorus–carbon bond formation using fluorous alkyl and aryl iodides [23,24]. The other involves the use of fluorous iodine(III) dichlorides for free radical chlorinations [25]. In this regard, phenyl iodine(III) dichloride (PhICl<sub>2</sub>) is an effective free radical chlorinating agent for hydrocarbons [26,27]. Importantly, the mechanism does not involve the liberation of Cl<sub>2</sub>, followed by the textbook sequence of steps. Rather, hydrogen abstraction is effected by a species other than the chlorine radical Cl·, presumably PhICl· [26,27].

One potential attraction of fluorous iodine(III) dichlorides as chlorinating agents would be the recovery and recycling of the fluorous iodide byproduct. Towards this end, higher fluorophilicities are usually advantageous. To a first approximation, these are maximized by increasing the lengths and quantities of the (CF<sub>2</sub>)<sub>n</sub> segments, and decreasing the lengths and quantities of any (CH<sub>2</sub>)<sub>m</sub> segments [1-3]. However, longer (CF<sub>2</sub>)<sub>n</sub> segments are often coupled with lower absolute solubilities [1,28], a logical consequence as one approaches the macromolecular limit of polytetrafluoroethylene. Fluorophilicities are typically quantified by fluorous/organic liquid/liquid phase partition coefficients [1-3]. The most common solvent combination is perfluoro(methylcyclohexane) (CF<sub>3</sub>C<sub>6</sub>F<sub>11</sub>) and toluene.

The objective of this study was to bridge several strategic gaps regarding highly fluorophilic building blocks for the formation of (1) phosphorus–carbon bonded species, and (2) iodine(III) dichloride reagents. For example, aliphatic species of the formula R<sub>f</sub><sub>n</sub>CH<sub>2</sub>CH<sub>2</sub>I are unstable [17]. However, analogs with one less methylene group, R<sub>f</sub><sub>n</sub>CH<sub>2</sub>I<sub>2</sub>, have been isolated for n = 8 and 10 as depicted in Scheme 1 [17,20]. Although partition coefficients are not available for the iodide R<sub>f</sub><sub>n</sub>CH<sub>2</sub>I (the byproduct that would form in most chlorination reactions),
they would fall between those of RfI (88.5:11.5 for CF3C6F11/toluene [29]) and Rf(CH2)2I (50.7:49.3 [30]). These rather modest fluorophilicities would presumably be lower for the more polar dichlorides Rf2CH2ICl2 – a possible disadvantage for reactions in fluoruous solvents. In any case, higher homologs that would have more biased partition coefficients were sought.

In the same vein, literature data prompted interest in certain fluoruous aromatic iodine(III) dichlorides. For example, the non-fluorous iodine(III) dichloride II-Me (Scheme 1) [31], which features two strongly electron-withdrawing nitro groups and a mildly electron-donating methyl group, is easily isolated in analytically pure form from the reaction of the corresponding aryl iodide and Cl2, even though the nitro groups render the iodine atom less Lewis basic and thermodynamically less prone to oxidation. The Hammett \( \rho \) values associated with CF3CF3 and CF2CF2CF3 substituents (\( \sigma_p 0.52; \sigma_m 0.47–0.52 \) [32]) suggest that Rf groups are less electron withdrawing than nitro groups (\( \sigma_p 0.81; \sigma_m 0.71 \)). Therefore, similar fluoruous compounds of the formula (Rf)2C6H3ICl2 were seen as realistic targets. The less fluorophilic homologs III and IV (Scheme 1), which feature three methylene or CH2CH2CH2 "spacers" that electronically insulate the arene ring from the perfluoroalkyl groups, have been previously isolated [17].

As described below, the pursuit of the preceding objectives has met with both success and some unanticipated speed bumps, for which parallel computational studies have provided valuable insight. Regardless, these efforts have resulted in a number of practical preparations that will soon be utilized in further applications [23], and defined various physical properties and stability limits that are useful guides for future research.

**Results**

**Syntheses and reactions, Rf6CH3I (n = 11, 13, 15).** To the authors’ knowledge, no fluoruous alkyl iodides of the formula Rf6CH3I are commercially available. Thus, as shown in Scheme 2, a sequence previously employed for lower homologs (\( n = 8, 10 \) [13]) was investigated. The commercially available alcohols Rf6CH2OH (\( n = 11, 13, 15 \)) were first converted to the triflates Rf6CH2OTf using pyridine and triflic anhydride (Tf2O) in (trifluoromethyl)benzene (CF3C6H3), an amphoteric solvent that is usually able to dissolve appreciable quantities of both fluoruous and non-fluorous solutes [33]. The reactions with \( n = 11 \) and 13 were conducted at 0 °C, and work-ups gave the expected triflates in 60–61% yields. In contrast, only traces of product were obtained with \( n = 15 \), presumably due to the poor solubility of the alcohol in virtually any medium. However, the solubilities of fluoruous compounds are often highly temperature dependent [28,34], and an analogous reaction at room temperature gave Rf15CH2OTf in 22% yield. The triflates were white solids with some solubility in acetone. They were characterized by IR and NMR (\( {1}H, {13}C\{1}H\), \( {19}F\{1}H\)) spectroscopy and microanalyses as summarized in the experimental section.

The triflates were treated with NaI in acetone at 75 °C. Over the course of 24 h, high conversions to the corresponding fluoruous iodosides Rf6CH2I were realized, although at rates much slower than with non-fluorous analogs. Work-ups afforded the products as analytically pure white solids in 58–69% yields, which were characterized analogously to the triflates. All were to some degree soluble in acetone, but as the perfluoroalkyl group lengthened, appropriate cosolvents were required to achieve significant concentrations. In order to obtain \( {13}C \) NMR spectra (\( n = 13, 15 \)), C6F6 – which is technically a non-fluorous solvent [35] but is nonetheless often effective with fluoruous solutes – was employed.

Importantly, these fluoruous aliphatic iodosides were more fluorophilic than those mentioned in the introduction. Representative partition coefficients were determined as described in the experimental section. Those for Rf15CH2I ranged from \( >99:<1 \) for CF3C6F11/toluene to 87:13 for CF3C6F11/aceton. The CF3C6F11/toluene partition coefficient of Rf15CH2I was also \( >99:<1 \). Next, CH3CN/C6F6 solutions of the fluoruous aliphatic iodosides (\( n = 11, 13 \)) were treated with aqueous NaOCl and conc. HCl. The combination of HCl and a mild oxidant generates Cl2, providing a "greener" synthetic approach to iodine(III) dichlorides [36-38]. Accordingly, the target molecules Rf6CH2ICl2 precipitated in 33–81% yields. However, the poor solubilities of these pale yellow powders precluded further purification by the usual protocols. Microanalyses confirmed the presence of chlorine.

![Scheme 2: Syntheses of fluoruous compounds of the formula Rf6CH2X.](image-url)
When $^1$H NMR spectra were recorded in acetone-$d_6$, new CH$_2$ signals 1.37–1.38 ppm downfield of those of the precursors R$_{10}$CH$_2$I were apparent. However, the NMR samples slowly became greenish yellow, suggestive of dissolved Cl$_2$, and the starting iodides were usually evident. The use of Cl$_2$ in place of NaOCl/HCl did not give better results.

**Syntheses and reactions, R$_{fO}$CH$_2$I ($x = 2–5$).** There is an ongoing effort in fluorous chemistry to decrease reliance on perfluoroctyl containing building blocks, which are associated with a variety of environmental issues [39]. One approach is to switch to related ethereal phase tags or "ponytails" [40,41]. Accordingly, oligomeric fluorous ethers that terminate in CH$_2$OH groups, CF$_3$CF$_2$CF$_2$O(CF(CF$_3$)CF$_2$O)$_x$CF(CF$_3$)CH$_2$OH, are commercially available. These are abbreviated R$_{fO}$CH$_2$OH, and the ethereal oxygen atoms have essentially no Lewis base character. In some cases, CF$_2$CF$_2$OCF(CF$_3$)CF$_2$OCF(CF$_3$)-segments have been found to impart higher fluorophilicites than similar perfluoroalkyl groups [42]. However, the multiple CF(CF$_3$) stereocenters are disadvantageous, as they render such compounds mixtures of diastereomers, presenting an impediment to crystallization. In some cases, NMR spectra do not differentiate the diastereomers, and in other cases more complex signal patterns are evident.

As shown in Scheme 3, the oligomeric alcohols ($x = 2–5$) were elaborated as described for the non-ethereal alcohols R$_{fN}$CH$_2$OH and a previous report involving the lower non-oligomeric homolog R$_{fO}$CH$_2$OH ($x = 1$ [5]). They were first converted to the triflates R$_{fO}$CH$_2$OTf using pyridine and triflic anhydride (Tf$_2$O). These were soluble in hexane/ethyl acetate and isolated as analytically pure colorless oils in 84–93% yields. Subsequent reactions with NaI in acetone (70–75 °C, $x = 2, 4, 5$) gave the corresponding iodides R$_{fO}$CH$_2$I as colorless liquids in 81–91% yields. Unfortunately, efforts to oxidize these compounds to the corresponding iodine(III) dichlorides using the conditions in Scheme 1 and Scheme 2 were unsuccessful. NMR analyses of crude reaction mixtures showed only starting material.

**Attempted syntheses of R$_{fN}$ICl$_2$.** Prior to the efforts described in the previous sections, iodine(III) dichlorides derived from perfluoroalkyl iodides R$_{fN}$I were considered as targets. Since these lack sp$^3$ carbon–hydrogen bonds, they are not susceptible to possible chlorination or other degradation under free radical chlorination conditions. However, no reactions were observed when R$_{fN}$I were treated with Cl$_2$ or NaOCl/HCl. Nonetheless, perfluoroalkyl iodides R$_{fN}$I ($n = 6–8, 10, 12$) can be oxidized using various recipes (e.g., 80% H$_2$O$_2$ in trifluoroacetic acid anhydride) to the iodine(III) bis(trifluoroacetates) R$_{fN}$I(OCOCF$_3$)$_2$ in high isolated yields [18,19,21]. It was thought that these might, in turn, react with TMSCl as sketched in Scheme 4 to provide “back door” entries to the target compounds R$_{fN}$ICl$_2$. Indeed, when these reactions were carried out, the samples exhibited the appropriate characteristic bright yellow colors ($n = 6, 8$). However, upon work-up only the original perfluoroalkyl iodides R$_{fN}$I were isolated. Hence, it is concluded that the target compounds are thermodynamically and kinetically unstable with respect to Cl$_2$ elimination, consistent with the failure of the direct reaction and a lower Lewis basicity of the iodine atom as compared to R$_{fN}$CH$_2$I.

![Scheme 3: Syntheses of fluorous compounds of the formula CF$_3$CF$_2$CF$_2$O(CF(CF$_3$)CF$_2$O)$_x$CF(CF$_3$)CH$_2$X'.](image-url)
After these experiments were carried out, we became aware of the isolation of CF$_3$ICl$_2$ (R$_f$IICl$_2$) from the reaction of CF$_3$ICIF and TMSCl at −40 °C [43]. This route is conceptually similar to that shown in Scheme 4, and a crystal structure of CF$_3$ICl$_2$ could even be obtained. However, consistent with our observations, the compound decomposed above −35 °C.

Syntheses and reactions, aryl iodides with one perfluoroalkyl group. Aromatic compounds are challenging to render highly fluorophilic [16,30,44]. For example, the singly-phase-tagged arene C$_6$H$_5$CH$_2$CH$_2$CH$_2$R$_{f8}$ gives a 49.5:50.5 CF$_3$C$_6$F$_{11}$/toluene partition coefficient. Values for doubly tagged analogs fall into the range (90.7–91.2):(9.3–8.8) (o, m, p-isomers), and that for the triply tagged species 1,3,5-C$_6$H$_3$(CH$_2$CH$_2$CH$_2$R$_{f8}$)$_3$ is >99.7:<0.3 [30]. As noted above, longer perfluoroalkyl segments increase fluorophilicities, as do shorter methylene segments (compare the partition coefficients of C$_6$H$_5$R$_{f8}$ (77.5:22.5) or 1,4-(R$_{f8}$)$_2$C$_6$H$_4$ (99.3:0.7) with the preceding examples [29]). Thus, in considering various fluorour aryliodine(III) dichloride targets, initial efforts were directed at systems with at least two R$_{f8}$ substituents per arene ring. Given the ready isolation of the dinitro-substituted aryliodine(III) dichloride II-Me in Scheme 1 [31], this was seen as a surefire objective.

However, this was not to be, so the results in this and the following section are presented in inverse chronological order, focusing first on arenes with one R$_{f8}$ substituent. As shown in Scheme 5 (top), the commercially available meta diiodide 1,3-C$_6$H$_4$I$_2$ was treated with copper (1.0 equiv) and R$_{f6}$I (0.5 equiv; a deficiency to help suppress dialkylation) in DMSO at 110 °C. Similar recipes have previously been used to couple aryl iodides and R$_{f6}$I building blocks [45,46]. Work-up gave the target compound 1,3-R$_{f6}$C$_6$H$_4$I in 60% yield (based upon limiting R$_{f6}$I).
Some of the previously reported dialkylation product 1,3-(R6H2)C6H4 was also formed [47,48], but was easily separated due to its differential fluorous lipophilicity (extraction of a CH2CN solution with perfluorohexane). An analogous procedure with Rf10I gave the higher homolog 1,3-Rf10C6H4I in 50% yield [9], and a lesser amount of what was presumed to be the dialkylation product. The analogous para diiodide 1,4-C6H4I2 gave parallel chemistry, as illustrated by the reaction with Rf6I to give 1,4-Rf6C6H4I (50% [4,12]) in Scheme 5 (bottom).

The three aryl iodides Rf6C6H4I thus obtained were treated with NaOCl/HCl per the sequence in Scheme 2. As shown in Scheme 5, work-ups gave the corresponding iodine(III) dichlorides Rf6C6H4ICl2 as pale yellow powders in 80–89% yields. Although these were clean by NMR, only one gave a correct microanalysis. As illustrated in Figure S1 (Supporting Information File 1), CDC13/C6F6 solutions of 1,3-Rf6C6H4ICl2 and 1,4-Rf6C6H4ICl2 containing an internal standard were monitored by 1H NMR. Slow partial evaporation of Cl2 to give the iodides 1,3-Rf6C6H4I and 1,4-Rf6C6H4I was observed (7% and 27% conversion over 60 h, respectively).

**Syntheses and reactions, aryl iodides with two perfluoroalkyl groups.** In a previously reported procedure [48], the diiodide 1,3-C6H4I2 was treated with copper (5.1 equiv) and Rf6I (2.2 equiv) in DMSO at 140 °C. As shown in Scheme 6 (top), the bis(perfluorohexyl) adduct 1,3-(Rf6)2C6H4, which was the undesired byproduct in Scheme 5 (top), was isolated at 75% yield. Subsequent iodination using NIS in fuming H2SO4/CF3CO2H afforded the "all meta" iodide 1,3,5-(Rf6)3C6H3I in 77% yield. The substitution pattern was evident from the 1H NMR spectrum. When Cl2 gas was sparged through a CF3C6H5 solution of 1,3,5-(Rf6)2C6H3I at −30 °C to −35 °C, the sample turned bright yellow. Two aliquots were removed. The 1H NMR spectrum of one (Figure 1b) showed two downfield shifted signals (cf. Figure 1a), which were attributed to the target molecule 1,3,5-(Rf6)2C6H3ICl2. Integration indicated 77:23 and 75:25 ArICl2/ArI ratios prior to and after solvent removal (room temperature, rotary evaporation). The isolated material was redisolved in CF3C6H5 and kept at −35 °C. After 7 d, the solvent was again removed by rotary evaporation, giving a 65:35 ArICl2/ArI mixture (Figure 1d). The solvent was removed from the second aliquot by oil pump vacuum at −40 °C. This gave a 35:65 ArCl2/Ar mixture as a pale white solid (Figure 1c). A variety of attempts to achieve higher conversions or isolate pure 1,3,5-(Rf6)2C6H3ICl2 were unsuccessful. It was concluded that 1,3,5-(Rf6)2C6H3ICl2 was much more labile with respect to Cl2 evolution than the fluorous aryliodine(III) dichlorides shown in Scheme 5, and that the 75–80% conversions reflected a thermodynamic limit.

Next, analogs of 1,3,5-(Rf6)2C6H3ICl2 with less electron-deficient iodine atoms were sought. As shown in Scheme 1, related fluorous aryliodine(III) dichlorides with three-methylene spacers, (Rf8CH2CH2CH2)2C6H3ICl2, had been isolated (the isomers III, IV) [17]. Recently, a potential precursor with two-methylene spacers, 1,3-(Rf8CH2CH2)2C6H3I4, became readily available [49]. Accordingly, it could be iodinated with I2/H2O6 as shown in Scheme 6 (bottom) to give 1,2,4-(Rf8CH2CH2)2C6H3I [50] in 93% yield after work-up. The 1H NMR spectrum clearly indicated the regiosomer in which the iodide is ortho and para to the two alkyl substituents. This contrasts with the iodination of 1,3-(Rf6)2C6H4I, in which the substituents function as meta directing groups.

As shown in Scheme 6, reactions of C6F6 or perfluoroheptane solutions of 1,2,4-(Rf8CH2CH2)2C6H3I and NaOCl/HCl gave the corresponding iodine(III) dichloride 1,2,4-
(Rf6CH2CH2)2C6H3ICl2 [50] as a white powder in 89% yield. This material was stable at room temperature and gave a microanalysis consistent with a monohydrate. Hence, the iodine atom in benzenoid compounds with two Rf6CH2CH2 substituents is sufficiently Lewis basic to support a dichloride, but analogs with two Rf6 substituents are not.

**Structural and computational data.** Crystal structures of fluorous compounds were virtually unknown 20 years ago [51], so opportunities to acquire structural data are usually seized. Crystals of 1,3,5-(Rf6)2C6H3I could be grown as described in the experimental section. X-ray data were collected, and the structure determined, as summarized in Table 1 and the experimental section. Two views of the molecular structure and key metrical parameters are provided in Figure 2. Two perspectives of the unit cell (Z = 8) are provided in Figure 3. There are some unusual features associated with the packing and space group, and these are treated in the discussion section.

In order to help interpret the accessibilities and/or stabilities of the various iodine(III) dichlorides described above, the gas phase free energies of chlorination were computed by DFT methods as described in the experimental section and summarized in Table S1 (Supporting Information File 1). The data are presented in "ladder format" in Figure 4, with the substrates that undergo more exergonic chlorinations placed higher. The energy difference between any pair of compounds is equal to that expressed by the corresponding isodesmic equation:

\[
\text{RI(g) or ArI(g) + Cl}_2(g) \rightarrow \text{RCl}_2(g) \text{ or ArCl}_2(g) \\
\text{RCl}_2(g) \text{ or ArCl}_2(g) + R'I(g) \rightarrow \text{ArCl}_2(g) + R'I'(g) \\
\]

The validity of the data was supported by the good agreement of the computed structure of 1,3,5-(Rf6)2C6H3I with the crystal structure (Figure 2). An overlay, provided in Figure S2 (Supporting Information File 1), shows only very slightly increasing conformational differences as the perfluorohexyl groups extend from the arene. For the aliphatic compounds (RfₙI, RfₙCH₂I, RfOCH₂ICl₂), the free energies of chlorination were calculated for a series of chain lengths. As summarized in Figure 4 and tabulated in Table S1 (Supporting Information File 1), the ΔG values within each series varied by less than 0.5 kcal/mol. In all cases, vertical ionization potentials (not presented) followed analogous trends.
Table 1: Summary of crystallographic data for 1,3,5-(Rf6)2C6H3I.

| Property                              | Value          |
|---------------------------------------|----------------|
| empirical formula                     | C18H3F26I      |
| formula weight                        | 840.10         |
| diffractometer                        | Bruker GADDS X-ray (three-circle) |
| temperature [K]                       | 110(2)         |
| wavelength [Å]                        | 1.54178        |
| crystal system                        | tetragonal     |
| space group                           | I4             |
| unit cell dimensions                  |                |
| a [Å]                                 | 29.6474(9)     |
| b [Å]                                 | 29.6474(9)     |
| c [Å]                                 | 5.5976(2)      |
| α [°]                                 | 90             |
| β [°]                                 | 90             |
| γ [°]                                 | 90             |
| V [Å³]                                | 4920.1(3)      |
| Z                                      | 8              |
| ρcalcd [Mg/m³]                        | 2.268          |
| µ [mm⁻¹]                              | 12.238         |
| F(000)                                | 3184           |
| crystal size [mm³]                    | 0.40 × 0.02 × 0.02 |
| θ limit [°]                           | 2.11 to 59.94  |
| index ranges [h, k, l]                | −33, 32; −33, 33; −6, 5 |
| reflections collected                 | 53384          |
| independent reflections               | 3568           |
| R(int)                                | 0.0540         |
| completeness (%) to θ (°)             | 99.8 (59.94)   |
| max. and min. transmission            | 0.7919 and 0.0843 |
| data/restraints/parameters            | 3568/1/407     |
| goodness-of-fit on F²                 | 0.991          |
| R indices (final) [I > 2σ(I)]         | 0.0156         |
| wR2                                   | 0.0355         |
| R indices (all data)                  | 0.0172         |
| wR2                                   | 0.0357         |
| largest diff. peak and hole [eÅ⁻³]    | 0.227 and −0.532 |

The iodine(III) dichlorides formed in the more exergonic reactions (upper portion of Figure 4) would be expected to be more stable with respect to Cl₂ evolution. Thus, the data are consistent with the stability order Rf₆CH₂ICl₂ >> Rf₆ICl₂ evident from Scheme 2 and Scheme 4. However, they also imply that the ethereal systems Rf₆CH₂ICl₂ (Scheme 3; −0.65 kcal/mol, x = 1) should be more stable than Rf₆CH₂ICl₂ (−0.53 to −0.59 kcal/mol, n = 4–8). All attempts to generate the former have been unsuccessful to date. Hence, there is either a kinetic barrier to the formation of Rf₆CH₂ICl₂ that is not overcome under the conditions of Scheme 3, or an unrecognized, presumably non-electronic, destabilizing feature.

In the same vein, there must be a mitigating factor, such as solubility, that allows the isolation of the dinitro-substituted aryl-iodine(III) dichloride II-Me in pure form (Scheme 1), but not the bis(perfluorohexyl) species 1,3,5-(Rf₆)₂C₆H₃ICl₂ (Scheme 6, Figure 1). The latter is derived from a more Lewis basic aryl iodide, with Cl₂ addition 0.83 kcal/mol more favorable. The ortho methyl group in II-Me plays a moderately stabilizing role, with Cl₂ addition to I-Me 0.73 kcal/mol more favorable than I. Otherwise, the computations (carried out with Rf₆ groups to aid comparability) nicely predict the relative stabilities of the fluorous aryliodine(III) dichlorides (1,2,4-(Rf₈CH₂CH₂)₂C₆H₄ICl₂ > 1,2,4-Rf₆C₆H₄ICl₂ > 1,3-Rf₆C₆H₄ICl₂).  

**Discussion**

The preceding experimental data define the stability limits associated with a broad range of fluorous aliphatic and aromatic
iodine(III) dichlorides. Aliphatic compounds of the formula \( \text{R}_n\text{ICl}_2 \) are clearly very unstable with respect to \( \text{Cl}_2 \) loss, although there is literature precedent for their synthesis and isolation from other iodine(III) precursors under exacting low temperature conditions [43]. When an insulating methylene group is introduced between the fluorous moiety and the \( \text{ICl}_2 \) group, the situation improves. Compounds of the formula \( \text{R}_n\text{CH}_2\text{ICl}_2 \) can generally be isolated, although they are somewhat labile towards \( \text{Cl}_2 \) loss. In contrast, efforts to prepare the ethereal systems \( \text{R}_n\text{OCH}_2\text{ICl}_2 \) by the chlorination of \( \text{R}_n\text{OCH}_2\text{I} \) have been unsuccessful. This poses a conundrum with respect to the DFT calculations; they seemingly possess sufficient Lewis basicity (Figure 4), but there appears to be a kinetic barrier.

In contrast, fluorous aromatic iodine(III) dichlorides bearing a single perfluoroalkyl group, \( \text{R}_{n6}\text{C}_6\text{H}_4\text{ICl}_2 \), are easily isolated in analytically pure form (Scheme 5), although they are still subject to slow \( \text{Cl}_2 \) loss in solution (Figure S1, Supporting Information File 1). However, it has not yet proved possible to quantitatively generate analogs with two perfluoroalkyl groups by chlorinations of iodine(I) precursors (Scheme 6, top); 75–80% conversions are the maximum realized to date. In contrast, chlorinations of the doubly substituted substrates \( \text{R}_{n6}(\text{CH}_2)_m\text{C}_6\text{H}_4\text{I} (m = 2, 3) \) go to completion, as exemplified in Scheme 1 (bottom) and Scheme 6 (bottom). The intervening methylene groups partially insulate the iodine atoms from the electron-withdrawing perfluoroalkyl segments, enhancing Lewis basicities.

However, it has not yet proved possible to access related compounds with three \( \text{R}_n\text{CH}_2\text{ICl}_2 \) groups, at least when two of them are ortho to the iodine atom, as exemplified by \( \text{V} \) in Scheme 1 [17]. To probe this point, the DFT calculations were extended to the \( \text{R}_{66} \text{ICl}_2 \) homologs of the precursors of the three arylidiodine(III) dichlorides in Scheme 1. These correspond to VII, VIII, and IX in Scheme 7 (top). The \( \Delta G \) values obtained were \(-3.40\), \(-3.75\), and \(-4.15 \text{ kcal/mol}\), respectively. Thus, the third \( \text{R}_n\text{CH}_2\text{I} \) substituent enhances the exergonicity of \( \text{Cl}_2 \) addition. Hence, the failure to observe a reaction must represent a kinetic phenomenon. A second "ladder", augmented with the additional alkyl and aryl iodides analyzed in the discussion section, is provided in Figure S3 (Supporting Information File 1).

Interestingly, isodesmic reactions corresponding to Equation 2 in the preceding section can actually be carried out. For example, \( \text{Cl}_2 \) can be transferred from the fluorous aliphatic
iodine(III) dichloride $R_{15}CH_2I$ to phenyl iodide as shown in Scheme 7 (middle) \[52\]. The $\Delta G$ value for the addition of $Cl_2$ to phenyl iodide is computed to be $-3.86 \text{ kcal/mol}$, as compared to $-0.72 \text{ kcal/mol}$ for $R_{15}CH_2I$. Curiously, the introduction of two $R_{15}(CH_2)_3$ substituents that are ortho/para or meta/para to iodine is thermodynamically deactivating for $Cl_2$ addition (VII/III and VIII/IV; $-3.40$ to $-3.75 \text{ kcal/mol}$), whereas the introduction of three that are ortho/para/ortho is activating (IX/V; $-4.15 \text{ kcal/mol}$) but kinetically inhibiting for steric reasons.

As noted in the introduction, a long-standing goal has been to realize highly fluorophilic aliphatic and aromatic iodine(I) compounds and iodine(III) dichlorides. The preceding results raise the question, "quo vadis?" When the compounds $R_{15}CH_2I$ and $R_{15}CH_2ICl_2$ reach $n = 15$ (Scheme 2), they are close to approaching a practical solubility limit, although the former gives a highly biased $CF_3C_6F_{11}/toluene$ liquid/liquid partition coefficient. Branched analogs may be more tractable. However, DFT calculations show that chlorinations of substrates such as $(R_{15})_3CCH_2I$ X (Scheme 7) would be strongly endergonic ($\Delta G = 3.36 \text{ kcal/mol}$, $n = 6$). Related species, such as (1) $(R_{15})_3CCF_2CF_2CH_2I$, which features a more remote branch site, or (2) $(R_{15}CH_2)_3CCH_2I$, which features additional insulating methylene groups, would be more likely to give stable iodine(III) dichlorides. Nonetheless, these types of species have never been described in the literature. Silicon has been used as a locus for branching, as exemplified by a variety of highly fluorophilic compounds of the formula $(R_{15}CH_2CH_2)_3SiZ$ (see XI in Scheme 7, $Z = 4-C_6H_5X$ \[53,54\]). However, these feature silicon–carbon and sp$^3$ carbon–hydrogen bonds that may be sensitive towards $Cl_2$. 

![Figure 3: Ball-and-stick and space filling representations of the unit cell of 1,3,5-$(Rf)_6C_6H_3I$.](image)

![Figure 4: Free energies of chlorination of relevant aryl and alkyl iodides to the corresponding iodine(III) dichlorides in the gas phase (kcal/mol), presented in a ladder format (each iodide is more Lewis basic than that shown below it).](image)
The fluorous aryl iodides that are precursors to III and IV have rather modest fluorophilicities (CF$_3$C$_6$F$_{11}$/toluene partition coefficients (69.5–74.7):(30.5–25.3) [16]), and simply lengthening the R$_f$ segments to R$_f^{10}$ or even longer is unlikely to achieve biases of >99:<1. The same goes for 1,2,4-(R$_f^8$CH$_2$CH$_2$)$_2$C$_6$H$_3$I in Scheme 6. Accordingly, we suggest that branched fluorous aryl iodides of the formula (R$_f^n$)$_3$CC$_6$H$_4$I (XII, Scheme 7) have particular promise. DFT calculations establish exergonic chlorinations, with $\Delta G$ values of $-1.93$ and $-1.59$ kcal/mol for $n = 6$ and 8. This implies that the corresponding iodine(III) dichlorides should have good stabilities, equal to or better than those of 1,3- and 1,4-R$_f^6$C$_6$H$_4$I in Scheme 5. However, this represents a currently unknown type of compound, and the synthesis is potentially challenging.

The following analysis of the crystal structure of 1,3,5-(R$_f^6$)$_2$C$_6$H$_3$I is kept brief, as this compound crystallizes in the same space group and crystal system (I4, tetragonal) as the corresponding bromide 1,3,5-(R$_f^6$)$_2$C$_6$H$_3$Br reported earlier [48]. The unit cell dimensions of the latter are virtually identical, with the cell volume ca. 1.5% lower (4851.7(4) vs 4920.1(3) Å$^3$), apropos to the smaller bromine atom. The space group is both chiral and polar, and the unit cell dimensions of both compounds feature c values (5.5976(2)–5.5624 Å) that are much smaller than the a and b values (29.6474(9)–29.5335(13) Å). As noted earlier and illustrated in Figure 2 (bottom), the sixteen perfluorohexyl groups associated with the eight molecules in the unit cell lie roughly in the a/b plane. They largely segregate, as seen for most fluorous molecules [44,51,55,56], into fluorous domains.

The eight arene rings in the unit cell tilt distinctly out of the a/b plane (average angle 49.1°). Furthermore, the eight iodine atoms are oriented on the same "side" or a/b face of the unit cell. In the neighboring unit cell that adjoins the a/b face, the iodine atoms are found on the opposite side (c direction). This represents the molecular basis for the polar nature of the crystal. Also, the C–C–C–C and F–C–C–F segments in the perfluorohexyl groups do not exhibit the idealized antiperiplanar and gauche conformations associated with saturated alkanes. Rather, the torsion angles for the roughly anti linkages average 164.4(1.6)° and 166.0(3.6)°, respectively. This leads to helical motifs as shown in Figure 5, which are furthermore reproduced by the computations. The basis for this deviation, as well as a more detailed presentation of the torsional relationships, is provided elsewhere [57-59]. In a given molecule, the C$_6$F$_{13}$ groups exhibit opposite helical chiralities (see Figure S2, Supporting Information File 1), affording a meso stereoisomer.
Finally, attempts have been made to extend the preceding chemistry in several directions. In screening experiments, all of the fluorous iodine(III) dichlorides assayed, as well as PhICl₂, were competent for the free radical chlorination of methane [25]. Under certain conditions, uncommon selectivities were apparent, but the fluorophilicities of the dichlorides or precursor iodides studied were insufficient for certain target recycling strategies. As discussed above, it is not clear how to meet these challenges at this time, although the couple R₁₁₂CH₂JCl₂/R₁₁₂CH₂I would be one of several with promise. Regardless, the fluorous iodides reported herein have numerous other uses, some of which will be communicated in the near future [23].

Conclusion
The preceding experimental and computational data have established a strong correlation between iodine atom Lewis basicity and the feasibility of oxidizing fluorous and non-fluorous aliphatic and aromatic iodides to the corresponding iodine(III) dichlorides. Although a few surprises are noted, these are attributed to special phenomena that can drive equilibria, such as precipitation (e.g., the conversion of I-Me to II-Me in Scheme 1), or kinetic barriers (inertness of R₀₂₆CH₂I in Scheme 3 or the precursor to V in Scheme 1). With the fluorous iodides, the extent of chlorination generally provides a measure of the degree to which the electron-withdrawing perfluoroalkyl or perfluoroether segments are insulated from the Lewis basic site.

Experimental
Five syntheses that are representative of the types of transformations in this study are detailed in the main article. The remaining preparations are described in Supporting Information File 1, together with data on the solvents, starting materials, and instrumentation employed.

R₁₁₁CH₂OTf. A Schlenk flask was flame dried, allowed to cool, charged with R₁₁₁CH₂OH (5.10 g, 8.52 mmol) and anhydrous CF₃COH (50 mL) under a N₂ flow, capped, and placed in an ice bath. Then pyridine (1.0 mL, 1.0 g, 13 mmol) and (after 30 min) Tf₂O (3.0 mL, 5.3 g, 14 mmol) were added dropwise by syringe with stirring. The ice bath was allowed to warm to room temperature. After 16 h, H₂O (60 mL) was added. After 30 min, the organic phase was separated and dried (MgSO₄). The solvent was removed by rotary evaporation. The residue was dissolved in petroleum ether/ethyl acetate (4:1 v/v). The solution was filtered through a silica pad (3 × 5 cm) and the solvent was removed by rotary evaporation to give R₁₁₁CH₂OTf as a white solid (3.82 g, 5.21 mmol, 61%), mp 77.2–79.9 °C (capillary). Anal. calcd for C₁₇H₁₇F₂₃ClO: C, 21.33; H, 0.28; F, 67.46; S, 4.38; found: C, 21.44; H, 0.31; F, 67.21; S, 4.15;

1H NMR (500 MHz, acetone-d₆) δ 5.55 (t, 3HF = 13 Hz, 2H, CH₂); 13C{¹H} NMR (470 MHz, acetone-d₆) δ 75.5 (s, 3F, −CF); 81.7 (t, JFF = 120.2 (m, 2F, CF₂), −122.2 (m, 12F, 6CF₂), −123.2 (m, 4F, 2CF₂), −126.7 (m, 2F, CF₂); ¹³C{¹H} NMR (125 MHz, acetone-d₆, partial) δ 70.0 (t, 2FCF = 28 Hz, CH₂); IR (powder film, cm⁻¹): 2924 (w), 2855 (w), 1418 (m), 1202 (s), 1140 (s), 1103 (w), 1023 (m), 854 (m), 822 (m).

R₁₁₁CH₂I. A round bottom flask was charged with R₁₁₁CH₂OTf (3.01 g, 4.11 mmol), NaI (10.2 g, 68.0 mmol), and acetone (30 mL), and fitted with a condenser. The flask was placed in a 75 °C oil bath and the mixture was stirred. After 1 d, the bath was removed and the mixture was allowed to cool. The solvent was removed by rotary evaporation. Then Et₂O (50 mL) and H₂O (40 mL) were added with stirring. After 5 min, the dark brown organic phase was separated, washed with saturated aqueous Na₂S₂O₃ until it became colorless, and dried (Na₂SO₄). The solvent was removed by rotary evaporation and the residue was dissolved in hexanes/ethyl acetate (20:1 v/v).

The solution was kept at −35 °C until a precipitate formed. The solid was collected by filtration and washed with cold hexanes to give R₁₁₁CH₂I as a white solid (2.00 g, 2.82 mmol, 69%), mp (capillary): 97.8–98.2 °C. Anal. calcd for C₁₇H₁₇F₂₃I: C, 20.30; H, 0.28; F, 61.54; I, 17.87; found: C, 20.20; H, 0.16; F, 61.29; I, 17.68; ¹H NMR (500 MHz, acetone-d₆) δ 4.06 (t, 3HF = 19 Hz,
2H, CH2); ^19F {1H} NMR (470 MHz, acetone-d6) δ = 81.6 (t, \( ^4J_{CF} = 10 \) Hz [60-62], 2F, CF2), −107.0 (m, 2F, CF2), −122.2 (m, 14F, 7CF2), −123.2 (m, 2F, CF2), −126.7 (m, 2F, CF2); ^13C {1H} NMR (125 MHz, acetone-d6, partial) δ = −3.8 (t, \( ^2J_{CF} = 25 \) Hz, CH2); IR (powder film, cm\(^{-1}\))]: 2986 (w), 2874 (w), 1422 (w), 1373 (w), 1348 (w), 1234 (s), 1204 (s), 1140 (s), 1046 (s), 858 (m).

**Rg11CH2IC12.** A round bottom flask was charged with Rg11CH2I (1.01 g, 1.42 mmol), C6F6 (1.4 mL), and CH3CN (14 mL) with stirring. Aqueous NaOCl (2.5% w/w, 21 mL) and then conc. HCl (10 mL) were slowly added. After 2 h, a pale yellow precipitate began to form. After 5 h, the mixture was filtered. The filter cake was washed with hexane (10 mL) and air dried (4–5 h) to give Rg11CH2IC12 as a pale yellow powder (0.90 g, 11.5 mmol, 81%), mp 122.1–125.4 °C (capillary). Analog. calc'd for C12H2F2Cl2I: C, 18.46%; H, 0.26%; F, 55.96%; Cl, 9.08%; found: C, 16.76%; H, 1.16%; F, 50.15% Cl, 7.98 [63]; ^1H NMR (500 MHz, CDCl3/C6F6) δ 8.54–8.52 (m, 2H), 7.94 (d, \( ^3J_{HH} = 8 \) Hz, 2H, CH2); ^19F {1H} NMR (470 MHz, acetone-d6, partial) δ =−106.7 (m, 2F, CF2), IR (powder film, cm\(^{-1}\))]: 107.0 (m, 2F, CF2), 122.3 (m, 2F, CF2), 127.3 (m, 2F, CF2).

**1,3-R6C6H4ICl2.** A round bottom flask was charged 1,3-R6C6H4I (0.523 g, 1.00 mmol), C6F6 (1 mL), and CH3CN (10 mL) with stirring. Aqueous NaOCl (2.5% w/w, 10 mL) followed by conc. HCl (10 mL) were slowly added. After 30 min, a pale yellow precipitate began to form. After 3 h, the mixture was filtered. The filter cake was washed with H2O (5 mL) and hexane (10 mL) and air dried (2 d) to give 1,3-R6C6H4ICl2 as a pale yellow powder (0.477 g, 0.804 mmol, 80%). Analog. calc'd for C12H6F13Cl2I: C, 24.31%; H, 0.68%; F, 41.65%; found: C, 23.89%; H, 0.38%; F, 49.81 [63]; ^1H NMR (500 MHz, CDCl3/C6F6) δ 8.54–8.52 (m, 2H), 7.94 (d, \( ^3J_{HH} = 8 \) Hz, 1H), 7.79 (t, \( ^3J_{HH} = 8 \) Hz, 1H), ^19F {1H} NMR (470 MHz, CDCl3/C6F6) δ =−82.3 (t, \( ^1J_{FF} = 9 \) Hz [60-62], 3F, CF3), −112.0 (t, \( ^1J_{FF} = 15 \) Hz [60-62], 2F, CF2), −124.4 (m, 4F, 2CF2), −123.7 (m, 2F, CF2), −127.3 (m, 2F, CF2).

**Partition coefficients.** The following is representative. A 20 mL vial was charged with a CF3C6F11 solution of Rg6CH2I (n = 11, 15; 5.0 × 10^{-2} M, 4.0 mL) and toluene (4.0 mL), capped, and vigorously stirred. After 10 min at room temperature (24 °C), aliquots were removed from the fluororous (2.0 mL) and organic (2.0 mL) phases. The solvent was evaporated from each, and the residues were dried under vacuum. A solution of Ph3SiMe3 (internal standard; 0.0055 mL) in acetone-d6/CF3/C6F6 (1:1 v/v; 10.0 mL) was prepared. Each residue was dissolved in 1.00 mL of this solution and ^1H NMR spectra were recorded. The relative peak integrations gave the corresponding partition coefficients.

**Crystallography.** A solution of 1,3,5-(R6)2C6H4I (ca. 0.05 g) in CHCl3/C6F6 (1.0 mL, 4:1 v/v) in an NMR tube was allowed to concentrate. After 2 d, colorless needles with well defined faces were obtained. Data were collected as outlined in Table 1. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2 [64]. Data were corrected for Lorentz and polarization factors, and using SADABS [65] for absorption and crystal decay effects. The structure was solved by direct methods using SHELXLT/XS [66,67]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model. The structure was refined (weighted least squares refinement on F^2) to convergence [66-68].

**Calculations.** Computations were performed with the Gaussian09 program package, employing the ultrafine grid...
(99,590) to enhance accuracy [69]. Geometries were optimized using density functional theory (DFT). The B3LYP [70-72] functional was employed with an all-electron 6-311+G(d,p) [73] basis set on all atoms except iodine, which was treated using an effective core potential, SDD [74]. The optimized structures were subjected to frequency calculations (using the same functional and basis set as before) to confirm that all structures were computational and basis set as before) to confirm that all structures were local minima and to obtain the free energies of chlorination (Figure 4 and Table S1, Supporting Information File 1).

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Supporting Information
Full details and product characterization for all the syntheses described in Schemes 2, 3, 5, and 6, information on the solvents, starting materials, and instrumentation employed, and additional spectroscopic, structural, and computational data, including a molecular structure file that can be read by the program Mercury [75] and contains the optimized geometries of all computed structures [76].

Supporting Information File 1
Experimental section continued.
[http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-13-246-S1.pdf]

Supporting Information File 2
Molecular structure file.
[http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-13-246-S2.mol2]
The recipe employed in this work is also a function of location, as Cl₂ is very difficult to obtain in Qatar. The recipe employed in this work is also a function of location, as Cl₂ is very difficult to obtain in Qatar.

See for recent lead references.

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