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Review

Polyvalent perfluoroorgano- and selected polyfluoroorgano-halogen(III and V) compounds

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ABSTRACT

This review compiles important aspects of the chemistry of polyvalent perfluoroorganohalogen(III and V) compounds of the last three decades and reports on distinctions which are worth mentioning in comparison with non-fluorinated polyvalent organohalogen(III and V) analogues. Besides general synthetic paths to neutral (R_FHalX_2, $(R_F)_2IX$, $(R_F)_3I$, and R_FHalX_4), cationic ($[R_F(R')Hal]Y$ and $[R_F(R')HalF_2]Y$), and anionic ($M[R_FHalX_3]$ and $M[(R_F)_2HalX_2]$) derivatives of iodine and bromine, transformations at the halogen centre of those polyvalent compounds and selected applications and their use as reagents are referred. Trends of ^{19}F and ^{13}C NMR spectroscopic properties of prototypes of polyvalent perfluoroorgano-iodine and -bromine compounds are compiled and interpreted. Structural features of characteristic perfluoroalkyl-, pentafluorophenyliodine(III and V), and few -bromine(III) compounds are presented and compared.

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1. Introduction

Polyvalent per- and polyfluoroorganohalogen(III and V) compounds are here considered as derivatives of the neutral halogen fluorides HalF$_n$ ($n \geq 3$) and their cationic and anionic species. Thus, we exclude two-coordinated derivatives of R_FI like $[(R_F)_2I]^-$, $[R_FIX]^-$, and R_FI·base adducts. Only polyvalent iodine and bromine(III and V) compounds are known as individuals up to now. Polyvalent halogen compounds with hypervalent bonds [1] mark one subgroup. Different kinds of bonds may be present in polyvalent halogen molecules, e.g. in $RHalX_2$ molecules with T-geometry and the VSEPR notation ABX_2E_2 (A = central halogen, B and X = ligands, E = electron lone pair) there are distinct bonds to R and X. The Hal-R bond is a 2c-2e bond whereas the linear X-Hal-X bond is a 3c-4e one. The latter Hal-X bonds are characterised by a bond order of 0.5 and a significant polar component with a distinctive partial positive charge on Hal and a negative one on X. Even RHal═O and other derivatives with a double bond to halogen in their Lewis formula possess hypervalent bonds.

During the last two decades a substantial number of reviews [2a–i] and some books [2j–n] dealt with polyvalent organoiodine compounds and their chemistry. Usually per- and polyfluoroorgano species were not in the focus of interest or they were excluded completely.

Within this review only polyvalent iodine and bromine compounds are considered which have at least one perfluorinated organo group (or a selected highly fluorinated organo group like a perfluoroalkyl group with a CH_2 spacer) directly attached to the halogen center.

2. Reaction routes to polyvalent per- and polyfluoroorganohalogen(III and V) compounds

The majority of described polyvalent per- and polyfluoroorganohalogen compounds are iodine(III) derivatives. The corresponding iodine(V) compounds are less represented in literature. To our knowledge, no polyvalent per- and polyfluoroorgano derivatives of iodine(VII) are known so far. Consequently, this chapter mainly deals with R_FIX_2 and R_FIX_4 and its cationic derivatives $[R_FRI]^+$ and $[R_FRF_2I]^+$. From the two anionic polyvalent iodine(III) species one was isolated and one was deduced from its NMR data in a product mixture of the reaction solution.

2.1. Per- and polyfluoroorganoiodine(III) compounds

The majority of reported R_FI(III) molecules can be described by the formula R_FIX_2. R_FIXY molecules represent a minority. The sparely known examples of $(R_F)_2IX$ and $(R_F)_3I$ molecules are discussed as reaction products of R_FIX_2 in Section 2.1.2.

2.1.1. Syntheses of per- and polyfluoroorganoiodine(III) molecules, R_FIX_2 and R_FIXY

One commonly applied access to R_FIX_2 molecules uses the oxidative addition of X_2 to R_FI. In this case X may be F, Cl, or OR. The monovalent iodine compound R_FI can be treated with the elements F_2 and Cl_2, with ROOR, or with formal sources of F, Cl or OR radicals. Reactions with elemental fluorine have to be performed in “inert” solvents like CCl_3F with diluted F_2 gas mixtures ($\leq 10\%$ F_2) at low temperatures, typically −78 °C (Eq. (1)). This approach was originally developed in 1959 by Schmeißer and Scharf [3] for CF_3IF_2 and later applied and modified for other perfluoroalkyl, perfluoroalkenyl, and perfluoroaryl iodides

$$R_FI + F_2(\text{diluted}) \xrightarrow{CCl_3F, -78\,^\circ C} R_FIF_2 \tag{1}$$

where $R_F = CF_3$ [3], C_2F_5, n-C_3F_7 [4], i-C_3F_7 [5], C_4F_9 [6], CF_2CF_2 [7], *cis*-, *trans*-$(CF_3)_2CFCF{=}CF$ [5], *cyclo*-C_6F_7 [8], C_6F_5 [9,10], 2,6-$C_6F_2H_3$ [11]. The precipitation of products, R_FIF_2, protects them against further fluorination to R_FIF_4.

The direct chlorination of perfluoroalkyl iodides to R_FICl_2 was not successful [12]. At this point we should remember that R_FI molecules have a partial positive charge on iodine in common. The addition of chlorine to R_FI needs activation (photochemically [13] or by the use of Lewis acids [14] (Eq. (2a)) as demonstrated in the case of C_6F_5I

$$C_6F_5I + Cl_2 \xrightarrow[CCl_3F, -78\,^\circ C]{[AlCl_3]} C_6F_5ICl_2 \tag{2a}$$

In contrast, polyfluoroalkyl iodides with one CH_2 unit as spacer between I and the C_nF_{2n+1} unit, form polyfluoroalkyliodine dichlorides by direct chlorine addition (Eq. (2b)) [15]

$$C_nF_{2n+1}CH_2I + Cl_2 \rightarrow C_nF_{2n+1}CH_2ICl_2 \tag{2b}$$

where $n = 1$–3.

Peroxo compounds ROOR allow the addition of two OR radicals to R_FI (Eq. (3))

$$R_FI + ROOR \rightarrow R_FI(OR)_2, \tag{3}$$

where $R_F = CF_3$, C_3F_7; R = $S(O)_2F$ [16].

As an alternative to elemental fluorine, the following fluorinating agents can be used for the conversion of R_FI to R_FIF_2: XeF_2 ($R_F = C_3F_7$ [17], C_4F_9 [18], CF_3CH_2 [18,19], C_6F_5 [17,20], 2,3,5,6-C_5F_4N [21]) $[C_6F_5XeF_2]^+$ ($R_F = C_6F_5$ [22]), ClF ($R_F = C_6F_5$ [10]), ClF_3 ($R_F = C_2F_5$, n- and i-C_3F_7, C_4F_9, C_6F_{13}, $C_{10}F_{21}$ [6,23,24]; BrF_3 ($R_F = C_4F_9$ [6,24]), $C_6F_5BrF_2$ ($R_F = C_6F_5$ [10]), BrF_5 ($R_F = C_2F_5$, C_4F_9 [6,24]), $C_6F_5BrF_4$ ($R_F = C_6F_5$ [10]), and $[(C_6F_5)_2IF_2]^+$ ($R_F = C_6F_5$ [25,26]). The action of halogen fluorides often results in a mixture of R_FIF_2 and R_FIF_4, and it was difficult to optimise the reaction conditions for the preparation of pure products. It is worth mentioning that the fluorinating ability of the mild fluoro oxidiser IF_5 is insufficient for fluorine addition to iodine in Alk_FI or in C_6F_5I [10]. In the latter case, the activation of IF_5 with BF_3 (Lewis acid) resulted in the addition of two fluorine atoms across one C═C double bond of C_6F_5I [8].

The formation of R_FIF_2 with ClF, ClF_3, and $ClOCF_3$ is described in the following equations

$$C_6F_5I + 2ClF \xrightarrow{CCl_3F, < -70\,^\circ C} C_6F_5IF_2 + Cl_2 \tag{4}$$

$$3R_FI + 2ClF_3 \xrightarrow{C_6F_{14}, \sim -78\,^\circ C} 3\,R_FIF_2 + Cl_2 \tag{5}$$

where $R_F = C_2F_5$, C_3F_7, C_4F_9, C_6F_{13}, $C_{10}F_{21}$.

$$R_FI + 2ClOCF_3 \rightarrow R_FIF_2 + Cl_2 + 2C(O)F_2 \tag{6}$$

where $R_FI = CF_3$ (without solvent, −70 °C [27]), C_6F_5 (CCl_3F, ≤ -78 °C [10]).

Another frequently used path to R_FIY_2 or R_FIXY compounds has a strong similarity to that presented by Eqs. (4) and (6), and is based on the addition of dipolar reagents XY (mainly, X = Cl). The products of addition reactions with $ClOCF_3$, $ClOC(CF_3)_3$, $ClONO_2$, $ClOS(O)_2F$, $ClOClO_3$, and Cl_2O strongly depend on the reaction conditions. Astonishingly, $CF_3I(Cl)F$ resulted as a product when a large excess of $ClOCF_3$ was applied (Eq. (7)) [28]. R_FI reacts with $\geq 2ClOC(CF_3)_3$ yielding $R_FI(OC(CF_3)_3)_2$ ($R_F = CF_3$, CF_2CF_2, $SF_5CF_2CF_2$, C_6F_5) (Eq. (8)) [29]. The reaction of CF_3I with 2 equiv. of $ClONO_2$ ended with a mixture of CF_3ICl_2, $CF_3I(Cl)ONO_2$, and $CF_3I(ONO_2)_2$ (Eq. (9a)) [30]. C_6F_5I and 4 equiv. of $ClONO_2$ formed the desired product $C_6F_5I(ONO_2)_2$ (Eq. (9b)) [31]. Primary perfluoroalkyl iodides react with $ClOS(O)_2F$ at low temperatures to give $R_FI(OS(O)_2F)_2$ (Eq. (10)) as an intermediate which after warming undergoes elimination of $IOS(O)_2F$ and results in $R_FOS(O)_2F$ [32]. In contrast, the secondary iodo compound $(CF_3)_2CFI$ forms the iodonium salt $[((CF_3)_2CF)_2I][I(OS(O)_2F)_4]$ under similar conditions [32]. No addition product was detected as an intermediate in reactions of R_FI with $ClOClO_3$. The consecutive product $[(R_F)_2I][I(OClO_3]_4]$ could be identified but decomposed finally to R_FOClO_3 [33]. In a similar manner the oxidative addition of OCl groups was performed when 2 equiv. of Cl_2O were added to C_6F_5I at −60 °C (Eq. (11)) [14]. $C_nF_{2n+1}I(OTeF_5)_2$ was obtained by addition of $ClOTeF_5$ (Eq. (12)). $CF_3I(OTeF_5)_2$ decomposed above −78 °C to give CF_3OTeF_5 [34]

$$CF_3I + ClOCF_3\,(\text{excess}) \rightarrow CF_3I(Cl)F + COF_2 \tag{7}$$

$$R_FI + 2ClOC(CF_3)_3 \rightarrow R_FI(OC(CF_3)_3)_2 + Cl_2 \tag{8}$$

$$CF_3I + 3ClONO_2 \rightarrow CF_3ICl_2 + CF_3I(Cl)ONO_2 + CF_3I(ONO_2)_2 \tag{9a}$$

$$C_6F_5I + 2ClONO_2 \rightarrow C_6F_5I(ONO_2)_2 + Cl_2 \tag{9b}$$

$$R_FI + 2ClOS(O)_2F \rightarrow R_FI(OS(O)_2F)_2 + Cl_2 \tag{10}$$

$$C_6F_5I + 2Cl_2O \rightarrow C_6F_5I(OCl)_2 + Cl_2 \tag{11}$$

$$C_nF_{2n+1}I + 2ClOTeF_5 \rightarrow C_nF_{2n+1}I(OTeF_5)_2 + Cl_2 \tag{12}$$

where n = 1–3.

The following routes from monovalent R_FI to trivalent R_FIX_2 combine individual oxidation steps with a metathesis and are used to synthesise perfluoroorganoiodine di(carboxylates), $R_FI(OC(O)R)_2$. The oxidation can be performed with ozone [35], HNO_3 [36], or a peroxoacid [12,37,38]. These reactions (Eqs. (13) and (14)) are very likely to proceed via the intermediate formation of R_FIO

$$\begin{aligned} &R_FI + 2HNO_3 + 2(CF_3C(O))_2O \\ &\quad \rightarrow R_FI(OC(O)CF_3)_2 + 2CF_3C(O)OH + 2NO_2 \end{aligned} \tag{13}$$

$$\begin{aligned} &R_FI + CF_3C(O)OOH + (CF_3C(O))_2O \\ &\quad \rightarrow R_FI(OC(O)CF_3)_2 + CF_3C(O)OH \end{aligned} \tag{14}$$

where $R_FI = Alk_FI, Aryl_FI, I(CF_2CF_2)_nI$.

Some representatives of R_FIO were prepared independently, and they may be considered as interesting starting materials for further $R_FI(III)$ compounds. However, the stability data of R_FIO should be interpreted carefully, e.g. violent explosions of C_6F_5IO at 60 °C (caution!) [39], significantly below the reported temperature of decomposition at 89 °C [36,40] or 210 °C [39], are documented in the literature. The direct addition of oxygen to R_FI with ozone is neither a simple nor a clean preparative route (Eq. (15)) [35] and failed in case of C_6F_5I [41]. Therefore, the hydrolysis of R_FIX_2 is a common way to R_FIO (see Section 3)

$$CF_3I + O_3 \xrightarrow{CCl_3F, \leq -40\,^\circ C} CF_3IO + O_2 \tag{15}$$

Generally, the nucleophilic introduction of per- and polyfluoroorgano groups is possible starting from suitable I(III) compounds, e.g. IF_3, ICl_3, $I(OC(O)CF_3)_3$, and $I(ONO_2)_3$. The substitution of one fluorine in IF_3 is not a favoured preparative route, because IF_3 only exists at low temperatures and disproportionates above −35 °C [42] finally forming I_2 and IF_5. Only one successful fluorine/perfluoroorgano group substitution reaction has been reported which used $Cd(C_6F_5)_2$ as reagent in EtCN at −78 °C (Eq. (16)). The yield of $C_6F_5IF_2$ was low (34%). Besides the by-products C_6F_5I (16%) and C_6F_5H (37%) the interesting molecule $(C_6F_5)_3I$ (3%) was observed as a trace product [43]

$$2IF_3 + Cd(C_6F_5)_2 \xrightarrow{EtCN, -78\,^\circ C} 2C_6F_5IF_2 + CdF_2 \tag{16}$$

$Cd(CF_3)_2\cdot$donor, $Cd(CF_3)X\cdot$donor, and $Bi(CF_3)_nX_{3-n}$ (n = 1–3) were offered as reagents for the nucleophilic introduction of trifluoromethyl groups into ICl_3, $I(OC(O)CF_3)_3$, and $I(ONO_2)_3$ (Eqs. (17) and (18)) [44]

$$IX_3 + Cd(CF_3)_2\cdot\text{donor} \rightarrow CF_3IX_2 + Cd(CF_3)X\cdot\text{donor} \tag{17}$$

$$IX_3 + Bi(CF_3)_3 \rightarrow CF_3IX_2 + Bi(CF_3)_2X \tag{18}$$

where X = Cl, $OC(O)CF_3$, ONO_2.

In the literature only one example is reported which shows that besides addition of fluorine to the iodine atom accessorily a substitution of H by F proceeded at the organo group and the alkyl iodide was finally transformed into the corresponding perfluoroorgano group (Eq. (19)) [45]

$$CH_3I + 2.5\,F_2 - N_2(1:20) \xrightarrow{CCl_3F, -110\,^\circ C} CF_3IF_2 + 3HF. \tag{19}$$

2.1.2. Syntheses of bis- and tris(perfluoroaryl)iodine(III) molecules $(Ar_F)_2IX$ and $(Ar_F)_3I$

To our knowledge, the family of $(Ar_F)_2IX$ and $(Ar_F)_3I$ compounds is represented by only two isolated species, $(C_6F_5)_2IF$ and $(C_6F_5)_3I$, which were characterised as individuals [46]. $(C_6F_5)_2IF$ was obtained on two routes (Eqs. (20) and (21)). The desired substitution of one hypervalently bonded fluorine in $C_6F_5IF_2$ was achieved with $Bi(C_6F_5)_3$ (3:1 molar ratio) in CH_2Cl_2. Alternatively, $(C_6F_5)_2IF$ precipitates after addition of NaF (in excess) to an aqueous solution of a suitable iodonium salt and can be isolated after extraction with CH_2Cl_2. $(C_6F_5)_2IF$ shows a high melting point of 202–204 °C and decomposes slowly in the melt. In water no hydrolysis proceeds. In aHF solution the iodonium polyfluoride salt $[(C_6F_5)_2I][F(HF)_n]$ is formed and after removal of aHF $(C_6F_5)_2IF$ was recovered completely

$$3C_6F_5IF_2 + Bi(C_6F_5)_3 \xrightarrow{CH_2Cl_2} 3(C_6F_5)_2IF + BiF_3 \tag{20}$$

$$[(C_6F_5)_2I][BF_4] + {>}\,1NaF \xrightarrow{H_2O} (C_6F_5)_2IF\downarrow + Na[BF_4]\downarrow \tag{21}$$

When $C_6F_5IF_2$ reacted with $Bi(C_6F_5)_3$ (slight excess, relative to the 3:2 stoichiometry, is necessary) in the basic solvent MeCN, $(C_6F_5)_3I$ was formed (Eq. (22)). In contrast to $(C_6F_5)_2IF$, $(C_6F_5)_3I$ shows two different types of C_6F_5 groups (^{19}F NMR): one in a 2c-2e mode and two (with a more anionic character) in a 3c-4e mode. The formation of $(C_6F_5)_3I$ as a by-product in the reaction of IF_3 with $Cd(C_6F_5)_2$ was mentioned above [43]

$$3C_6F_5IF_2 + {>}\,2Bi(C_6F_5)_3 \xrightarrow{MeCN} 3(C_6F_5)_3I + 2BiF_3. \tag{22}$$

2.1.3. Per- and polyfluoroorganoiodonium(III) salts $[R_F(R')I]Y$ and $[R_F(X)I]Y$

Routes to iodonium salts, $[R(R')I]Y$ or $[R(X)I]Y$, with one or two C–I bonds in the cation can principally proceed from precursors with the same number of C–I bonds, e.g. by abstraction of a negatively charged ligand X from the I(III) molecules $R(R')IX$ or RIX_2 (Eq. (23a)) or by addition of an electrophile, preferable a proton to a I═O or I═C double bond (Eq. (23b)), or by reduction of the corresponding organoiodine(V) precursor (Eq. (23c)). Additionally, the transformation (including fluorination) of one or both organo group(s) bonded to I(III) (Eq. (23d)) has to be mentioned

$$R(R')IX \text{ or } RIX_2 + LA \rightarrow [R(R')I][LA\text{-}X] \text{ or } [R(X)I][LA\text{-}X] \tag{23a}$$

$$\mathrm{RI{=}O\ or\ RI{=}C(R')_2 + HY \rightarrow [RI(OH)]Y\ or\ [RI(CH(R')_2)]Y} \qquad (23b)$$

$$\mathrm{R(R')IX_3 + 2e^- \rightarrow [R(R')I]X + 2X^-} \qquad (23c)$$

$$\mathrm{[R(R')I]Y \rightarrow [R(R'')I]Y\ or\ [R''(R''')I]Y} \qquad (23d)$$

In case of perfluorinated iodonium salts the routes in (Eqs. (23a)–(23c)) describe no useful paths and no example of route (Eq. (23d)) has been reported so far. The perfluoroorganyliodonium salts $[R_FIX]Y$ (X = F, $OC(O)CF_3$, etc.) or structurally related species (Eq. (23a)) were discussed as intermediates in reactions of R_FIX_2 with Lewis acids. Yagupol'skii et al. observed the precipitation of a product "$[R_FIF][BF_4]$" when BF_3 was bubbled into the dichloromethane solution of R_FIF_2 ($R_F = C_3F_7$, C_6F_{13}) at low temperatures, but they did not study the nature of this solid [47]. The protonation of $C_6H_5I{=}C(SO_2X)_2$ (X = F, CF_3) with HOTf in CH_2Cl_2 resulted in a solution of $[C_6H_5(CH(SO_2X)_2)I][OTf]$, while under the same conditions, the corresponding pentafluorophenyl derivative, $[C_6F_5(CH(SO_2F)_2)I][OTf]$, was detected only as a minor component of a complex mixture by ^{19}F NMR [48]. The dissolution of C_6F_5IO in cold (−50 °C) HSO_3F was described rather as the donor-acceptor complex $[C_6F_5I{=}O{\cdot}HOSO_2F]$ than as the salt $[C_6F_5(OH)I][OSO_2F]$. In the stronger acid (HSO_3F–SbF_5) C_6F_5IO decomposed and iodine was formed [49].

Perfluoroorganoiodonium salts $[R_F(R')I]Y$ with all kinds of organo groups were preferentially prepared by methods which enable the formation of a second carbon–iodine bond. Some of the applied methods are common procedures whereas others are less familiar.

The formal addition of a carbocation characterises one approach. Thus, the salt $[CF_3(CH_3)I][MF_6]$ was obtained by the electrophilic methylation of CF_3I with CH_3F and MF_5 in SO_2 (Eq. (24a)) [50]. Mono- and di-methylation of 1,4-diiodotetrafluorobenzene occurred similarly (Eq. (24b)) [51]:

$$\mathrm{CF_3I + CH_3F + MF_5 \xrightarrow{SO_2,-78\,^\circ C} [CF_3(CH_3)I][MF_6]\ (M = As, Sb)} \qquad (24a)$$

$$\mathrm{1,4\text{-}C_6F_4I_2 + CH_3F + SbF_5 \xrightarrow[-78\,^\circ C]{SO_2} [4\text{-}IC_6F_4(ICH_3)][SbF_6] + [1,4\text{-}C_6F_4(ICH_3)_2][SbF_6]_2} \qquad (24b)$$

Perfluoroalkynylxenonium tetrafluoroborates displayed excellent alkynylating properties in reactions with alkyl-, trifluorovinyl-, and fluoroaryl-iodides (Eq. (25)) [52]

$$\mathrm{[CF_3C{\equiv}CXe][BF_4] + R'I \xrightarrow[-30\ to\ 20\,^\circ C]{aHF} [CF_3C{\equiv}C(R')I][BF_4] + Xe} \qquad (25)$$

where R′ = CF_3CH_2, $CF_2{=}CF$, C_6F_5, 3-FC_6H_4.

The synthesis of $[(C_6F_5)_2I][AsF_6]$ was successfully performed in the high viscous melt of salt $[C_6F_5Xe][AsF_6]$ with a 10-fold excess of C_6F_5I at 140 °C (Eq. (26)) [40]

$$\mathrm{C_6F_5I(excess) + [C_6F_5Xe][AsF_6] \xrightarrow[melt,1\,h]{140\,^\circ C} \underset{20\%}{[(C_6F_5)_2I][AsF_6]} + Xe^0} \qquad (26)$$

Both reactions, (25) and (26), and the formation of $[(C_6F_5)_2I][(C_6F_5)_3BF]$ from C_6F_5I and $[C_6F_5Xe][(C_6F_5)_3BF]$ in acetonitrile solution at 20 °C [53] occurred in an electrophilic pathway. Further investigations showed however that the related salts, $[C_6F_5Xe]Y$ (Y = $[AsF_6$, $C_6F_5BF_3]$), did not react with iodopentafluorobenzene (MeCN, 20 °C, 70 h; MeCN, 80 °C, 4 h; CH_2Cl_2, 80 °C, 4 h [40]). It can be assumed that the pentafluorophenylation of C_6F_5I occurred via the electrophilic pentafluorophenyl radical generated by the thermal decomposition of $[C_6F_5Xe][AsF_6]$ (in the melt) or $[C_6F_5Xe][(C_6F_5)_3BF]$ (in solution). The inertness of C_6F_5I to [2,4,6-$C_6F_3H_2Xe][BF_4]$ in MeCN at 20 °C and the formation of [2,4,6-$C_6F_3H_2(C_6F_5)I][BF_4]$ at 60 °C [54] can be explained in the same way.

The generation of an organyliodine(III) electrophile and the subsequent reaction with an appropriate aromatic compound ArH provided an effective access to per- and polyfluorinated organyl(aryl)iodonium salts and was first described by Yagupol'skii and co-workers [55]. The first step in this sequence involves the polarization, e.g. (a) of one I–F bond in R_FIF_2 by BF_3 (Eq. (27) or (b) of one I–O bond by protonation of the oxygen-containing acyloxy ligand directly bonded to I(III) (Eq. (28)):

$$\mathrm{R_FIF_2 + BF_3 \rightarrow \langle R_FIF\text{-}\text{-}FBF_3\rangle \xrightarrow[-HF]{ArH} [R_F(Ar)I][BF_4]} \qquad (27)$$

$$\mathrm{R_FI(OC(O)R')_2 \xrightarrow{H^+} [R_FIOC(O)R'(OC(OH)R')]^+ \xrightarrow[-HOC(O)R']{ArH} [RF(Ar)I][OC(O)R']} \qquad (28)$$

The generation of the electrophile according to (Eq. (29)) occurred when bubbling BF_3 into the cold (−60 °C) solution of R_FIF_2 in CH_2Cl_2 or $CHCl_3$, whereupon a precipitate was formed. The subsequent addition of benzene or toluene at 20 °C yielded the iodonium salt $[R_F(Ar)I][BF_4]$ [47]. α,ω-Bis(aryliodonium)perfluoroalkylene salts were obtained similarly (Eq. (30)) [38]

$$\mathrm{R_FIF_2 + BF_3 \xrightarrow[2.C_6H_6,-60\ to\ 20\,^\circ C]{1.CH_2Cl_2,-60\,^\circ C} \underset{>90\%}{[R_F(C_6H_5)I][BF_4]}} \qquad (29)$$

where $R_F = C_3F_7$; C_6F_{13}

$$\mathrm{F_2I(CF_2CF_2)_{\mathit{n}}IF_2 + 2C_6H_6 + 2BF_3 \xrightarrow[2.C_6H_6,-60\ to\ 20\,^\circ C]{1.CH_2Cl_2,-60\,^\circ C} \underset{57-62\%}{[C_6H_5I(CF_2CF_2)_{\mathit{n}}IC_6H_5][BF_4]_2}} \qquad (30)$$

where n = 2, 3. The electrophilic iodopentafluophenylation of mesitylene was performed in high yield under modified conditions (Eq. (31)) [5]

$$\mathrm{C_6F_5IF_2 + BF_3{\cdot}NCCH_3 \xrightarrow[2.\,1,3,5-C_6H_3(CH_3)_3]{1.MeCN,-40\,^\circ C} \underset{90\%}{[C_6F_5(2,4,6\text{-}C_6H_2(CH_3)_3)I][BF_4]}} \qquad (31)$$

The solution of per- and polyfluoroalkyliodine bis(trifluoroacetate) in $CF_3C(O)OH$ reacted with benzene and toluene at 0 °C to give per- and polyfluoroalkyl(aryl)iodonium trifluoroacetate. The latter can be converted into the corresponding halides [37,55]. Pentafluorophenyliodonium salts were obtained analogously (Eq. (32))

$$\mathrm{R_FI(OC(O)CF_3)_2 + ArH \xrightarrow[2.MY,-M[OC(O)CF_3]]{1.CF_3C(O)OH,0\,^\circ C,60-100\,h} [R_F(Ar)I]Y} \qquad (32)$$

where $R_F = C_3F_7$, C_6F_{13}, $H(CF_2CF_2)_2CH_2$, $H(CF_2CF_2)_3CH_2$, C_6F_5; Ar = C_6H_5; $CH_3C_6H_4$; MY = AgF in MeCN, aqueous NaCl or aqueous $[Et_4N]Br$.

It is interesting that the reactivity of $(CF_3C(O)O)_2I(CF_2CF_2)_nI(OC(O)CF_3)_2$ towards ArH diminishes with the elongation of the carbon chain from n = 1 to 3. The ethane derivative (n = 1) reacted with benzene to yield the corresponding diiodonium salt, whereas the reaction with toluene occurred too rigorous and gave tar. The butane derivative (n = 2) did not react with C_6H_6 whereas the reaction with $C_6H_5CH_3$ was completed after 14 d. The hexane derivative (n = 3) did neither react with benzene nor with toluene [38] (Eq. (33))

$$\mathrm{(CF_3C(O)O)_2I(CF_2CF_2)_{\mathit{n}}I(OC(O)CF_3)_2 + ArH \xrightarrow[25\,^\circ C]{CF_3C(O)OH} [ArI(CF_2CF_2)_{\mathit{n}}IAr][OC(O)CF_3]_2} \qquad (33)$$

where n = 1, Ar = C_6H_5; n = 2, Ar = 4-$CH_3C_6H_4$.

Umemoto et al. improved this method significantly by using the stronger protic acids (HOTf, $HOS(O)_2F$ or H_2SO_4) instead of $CF_3C(O)OH$ [56,57]. Under these conditions, the reaction of perfluoroalkyliodine bis(trifluoroacetates) with benzene or fluorobenzene was completed within 1 d to give perfluoroalkyl(aryl)iodonium salts in high yields (Eqs. (34a)–(34c))

$$R_FI(OC(O)CF_3)_2 + C_6H_6 + HY \xrightarrow[0\,^\circ C,\,1\,d]{CF_2ClCFCl_2} \underset{>90\%}{[R_F(C_6H_5)I]Y} + 2CF_3C(O)OH \tag{34a}$$

where $R_F = C_nF_{2n+1}$ (n = 2, 3, 4, 6, 7, 8, 10), $(CF_3)_2CF$, CF_2BrCF_2, $H(CF_2)_{10}$

$$R_FCH_2I(OC(O)CF_3)_2 + C_6H_6 + HY \xrightarrow[0\,^\circ C,1\,d]{CF_2ClCFCl_2} \underset{70-90\%}{[R_FCH_2(C_6H_5)I]Y} + 2CF_3C(O)OH \tag{34b}$$

where $R_F = CF_3$, C_3F_7, C_7F_{15}, $H(CF_2)_{10}$, HY = HOTf, $HOS(O)_2F$, H_2SO_4

$$(CF_3C(O)O)_2I(CF_2)_mI(OC(O)CF_3)_2 + C_6H_6 + HOTf \xrightarrow[0\,^\circ C,1\,d]{CF_2ClCFCl_2} \underset{90-95\%}{[C_6H_5I(CF_2)_mIC_6H_5][OTf]_2} + 2CF_3C(O)OH \tag{34c}$$

where m = 3, 8.

Furthermore, poly- and even perfluorinated diaryliodonium salts could be prepared by this method as demonstrated by the synthesis of bis(2,6-difluorophenyl)iodonium triflate [11] (Eq. (35)) and bis(pentafluorophenyl)iodonium triflate. The latter was obtained directly from pentafluorobenzene and iodine tris(trifluoroacetate) in the presence of HOTf. It is likely that the reaction proceeds via $C_6F_5I(OC(O)CF_3)_2$ [58] (Eq. (36))

$$2,6\text{-}C_6F_2H_3I(OC(O)CF_3)_2 + 1,3\text{-}C_6F_2H_4 + HOTf \xrightarrow[20\,^\circ C,48\,h]{CF_3C(O)OH} \underset{80\%}{[(2,6\text{-}C_6F_2H_3)_2I][OTf]} \tag{35}$$

$$2C_6F_5H + I(OC(O)CF_3)_3 + HOTf \xrightarrow[20\,^\circ C,72\,h]{CF_3C(O)OH} \underset{81\%}{[(C_6F_5)_2I][OTf]} \tag{36}$$

A useful approach to polyfluoroalkyl(aryl)iodonium sulfonates and polyfluoroalkyl(alkynyl)iodonium sulfonates was elaborated by Zhdankin et al. [59–61]. They found out that 1-[hydroxy(sulfonyloxy)iodo]-1*H*,1*H*-perfluoroalkanes (see Section 3, Eq. (77)) smoothly react with aryltrimethylsilanes and alkynyltrimethylsilanes under very mild conditions to give iodonium salts in high yields. In contrast to the methods discussed above, this procedure does not require the presence of acids and can be employed in case of acid-sensitive substrates (Eqs. (37a) and (37b))

$$C_nF_{2n+1}CH_2I(OH)Y + ArSiMe_3 \xrightarrow[-30\,to\,0\,^\circ C,2\,h]{CH_2Cl_2} [C_nF_{2n+1}CH_2(Ar)I]Y + 0.5(Me_3Si)_2O + 0.5H_2O \tag{37a}$$

where n = 1, 2; Ar = C_6H_5, 2-MeC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$Me_3SiC_6H_4$, 4-ClC_6H_4; Y = OTf, OTs

$$C_nF_{2n+1}CH_2I(OH)OTf + R''C{\equiv}CSiMe_3 \xrightarrow{CH_2Cl_2} [C_nF_{2n+1}CH_2(R''C{\equiv}C)I][OTf] + 0.5(Me_3Si)_2O + 0.5H_2O \tag{37b}$$

where n = 1(−30 to 0 °C, 2 h), n = 2 (reflux, 2 h), R″ = Ph, *t*-Bu, Me_3Si.

In contrast, 1-[hydroxy(sulfonyloxy)iodo]perfluoroalkanes, $C_nF_{2n+1}I(OH)OTf$, were less reactive and did not react with alkynyltrimethylsilanes. Iodoperfluoroalkyldesilylation of aryltrimethylsilanes with Y = $OS(O)_2CF_3$ proceeded in the presence of Me_3SiOTf, whereas the reactions with Y = $OS(O)_2CH_3$) and Y = 4-$OS(O)_2C_6H_4CH_3$) were much slower even in the presence of $CF_3C(O)OH$ (3–4 equiv.) (Eq. (37c)) [59,60]

$$C_nF_{2n+1}I(OH)OTf + ArSiMe_3 \xrightarrow[-78\,to\,20\,^\circ C]{Me_3SiOTf,CH_2Cl_2} [C_nF_{2n+1}(Ar)I][OTf] + 0.5(Me_3Si)_2O + 0.5H_2O \tag{37c}$$

where n = 2, 3, 4, 6, 8; Ar = C_6H_5, 2-MeC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$Me_3SiC_6H_4$, 4-ClC_6H_4.

Usually, reactions of polyfluoroorganyliodine(III) electrophiles derived from R_FIX_2 with ArH, $ArSiMe_3$, and $R''C{\equiv}CSiMe_3$ are very attractive for the preparation of asymmetric iodonium salts $[R_F(R)I]Y$ (R = Ar, $R''C{\equiv}C$). This route is restricted to sufficiently nucleophilic partners ArH or aryl- and alkynyltrimethylsilanes, because of the relative weakness of the iodine electrophiles applied here.

A convenient approach to per- and polyfluorinated iodonium salts is based on the reaction of organyliodine(III) difluoride with organoboranes, RBX_2. Initially, this reaction was performed with triarylboranes (X = R) and resulted in diaryliodonium arylfluoroborates (Eqs. (38a) and (38b)) [53,43,62]. Later, Naumann et al. performed it in the presence of $BF_3{\cdot}OMe_2$, and thus obtained the corresponding tetrafluoroborates (Eq. (38c)) [54,11]

$$C_6F_5IF_2 + B(C_6F_5)_3 \xrightarrow{solvent} [(C_6F_5)_2I][(C_6F_5)_nBF_{4-n}] (n = 0-4) \tag{38a}$$

Solvent: CH_2Cl_2 (−50 °C, 1 h) or MeCN (−40 °C, 4 d) [53,62]

$$IF_3 + B(C_6F_5)_3 \xrightarrow[-78\,^\circ C]{CH_2Cl_2} \underset{68\%}{[(C_6F_5)_2I][(C_6F_5)_nBF_{4-n}]} (n = 0-3) \tag{38b}$$

$$3R_FIF_2 + BAr_3 + 2\,BF_3 \cdot OMe_2 \xrightarrow[-40\,^\circ C,24\,h]{CH_2Cl_2} 3[R_F(Ar)I][BF_4] \tag{38c}$$

where $R_F = C_6F_5$, 2,6-$C_6F_2H_3$; Ar = 2-FC_6H_4, 3-FC_6H_4, 4-FC_6H_4, 2,6-$C_6F_2H_3$, 2,4,6-$C_6F_3H_2$, C_6F_5.

A straightforward preparative approach to per- and polyfluoroorganodifluoroboranes R_FBF_2 ($R_F = C_6F_nH_{5-n}$, R″CF = CF, CF_2 = CR″, $R''C{\equiv}C$) in weakly coordinating solvents (CH_2Cl_2, 1,1,1,3,3-pentafluoropropane (PFP), 1,1,1,3,3-pentafluorobutane (PFB)) was developed by Frohn and Bardin in the last decade [63,64] and allowed the syntheses of a number of symmetric and asymmetric bis(per- and polyfluoroaryl)iodonium (Eqs. (39a) and (39b)) [65,21,66], perfluoroalkenyl(aryl)iodonium (Eq. (39c)) [21,66], perfluoroalkynyl(aryl)iodonium, perfluoroalkynyl(perfluoroalkenyl)iodonium, perfluoroalkynyl(polyfluoroalkyl)iodonium (Eq. (39d)) [18], and perfluoroalkyl(perfluorophenyl) iodonium [5,67] tetrafluoroborates (Eq. (39e))

$$C_6F_5IF_2 + ArBF_2 \xrightarrow[0\,to\,22\,^\circ C]{CH_2Cl_2} [C_6F_5(Ar)I][BF_4] \tag{39a}$$

where Ar = C_6H_5, 2-FC_6H_4, 3-FC_6H_4, 4-FC_6H_4, 2,6-$C_6F_2H_3$, 3,5-$C_6F_2H_3$, 2,4,6-$C_6F_3H_2$, 3,4,5-$C_6F_3H_2$, C_6F_5, 4-C_5F_4N

$$(4\text{-}C_5F_4N)IF_2 + (4\text{-}C_5F_4N)BF_2 \xrightarrow[0\,^\circ C,10\,min]{CH_2Cl_2} [(4\text{-}C_5F_4N)_2I][BF_4] \tag{39b}$$

$$R'IF_2 + R''CF{=}CFBF_2 \xrightarrow[-60\,^\circ C]{CH_2Cl_2} \underset{70-95\%}{[R'(R''CF{=}CF)I][BF_4]} \tag{39c}$$

where R′ = C_6H_5, 2-FC_6H_4, 3-FC_6H_4, 4-FC_6H_4, C_6F_5, R″ = F, *trans*-CF_3

$$R_FIF_2 + R''C{\equiv}CBF_2 \xrightarrow[-60\,to\,-10\,^\circ C,\,34\,d]{PFP\,or\,CH_2Cl_2} \underset{74-90\%}{[R_F(R''C{\equiv}C)I][BF_4]} \tag{39d}$$

where $R_F = C_6F_5, (CF_3)_2CFCF = CF, C_4F_9, CF_3CH_2$; $R'' = (CH_3)_3C, CF_3, (CF_3)_2CF$

$$C_6F_5BF_2 + C_6F_{13}IF_2 \xrightarrow[0\,^\circ C]{CCl_3F} [C_6F_5(C_6F_{13})I][BF_4] \tag{39e}$$

The transfer of the organo group from boron to iodine(III) follows a Lewis acid–Lewis base interaction (Scheme 1). Two aspects are important for such acid-assisted nucleophilic substitutions: (a) the interaction of the acid RBX_2 with the IF_2 triad weakens one I–F bond and makes the iodine centre more electrophilic and (b) as a consequence of the interaction of the fluoro base with the acid RBX_2, the nucleofugality of the R group will increase.

Recently, phenylphosphorus(V) tetrafluoride was also successfully used for the preparation of fluoroaryl(phenyl)iodonium hexafluorophosphates (Eq. (40)) [21]

$$ArIF_2 + C_6H_5PF_4 \xrightarrow[-60\,^\circ C]{CH_2Cl_2} [Ar(C_6H_5)I][PF_6] \tag{40}$$

where $Ar = C_6F_5$, 4-FC_6H_4.

In the presence of the strong Lewis acid, NbF_5, polyfluorophenyl groups are transferred from triarylbismuth to fluoroaryliodine(III) difluoride and diaryliodonium salts are formed in high yields (Eq. (41)) [68]

$$3ArIF_2 + 3NbF_5 + Bi(Ar')_3 \xrightarrow[-40\ \text{to}\ 20\,^\circ C]{MeCN} 3\,\underset{85-91\%}{[Ar(Ar')I][NbF_6]} + BiF_3 \tag{41}$$

where $Ar = C_6F_5$, $Ar' = 2,6\text{-}C_6F_2H_3, C_6F_5$; $Ar = 2,6\text{-}C_6F_2H_3$, $Ar' = 2,4,6\text{-}C_6F_3H_2$.

Finally, reactions with a less general interest in the syntheses of polyfluoroorganyliodonium salts are reported. The bis(pentafluorophenyl)iodonium salt was obtained from $C_6F_5SiF_3$ and $[IF_4][SbF_6]$ in HSO_3F. During this conversion $C_6F_5IF_4$, one of the possible intermediates, could not be detected [69].

The most remarkable property of iodosylbenzene C_6H_5IO is the ability to disproportionate under controlled thermal conditions (steam distillation) yielding $C_6H_5IO_2$ and C_6H_5I. In contrast, its perfluorinated analogue, C_6F_5IO, formed the iodonium salt under similar conditions (Eq. (42)) [40]

$$3C_6F_5IO \xrightarrow[100\,^\circ C, 6\,h]{} \underset{60\%}{[(C_6F_5)_2I][IO_3]} + C_6F_5I \tag{42}$$

Pentafluorophenyl(phenyl)iodonium chloride was obtained by the nucleophilic arylation of $PhICl_2$ with C_6F_5Li and then converted into the more stable trifluoroacetate (Eq. (43)) [9]

$$\begin{aligned} &C_6H_5ICl_2 + C_6F_5Li \xrightarrow[-78\ \text{to}\ 20\,^\circ C]{ether} \underset{23\%}{[C_6F_5(C_6H_5)I]Cl} \\ &\xrightarrow[\text{reflux, 3 h}]{CF_3C(O)OH(CF_3C(O))_2O} [C_6F_5(C_6H_5)I][OC(O)CF_3] \end{aligned} \tag{43}$$

A few communications deal with bis(perfluoroalkyl)iodonium salts. Generally, the formation of onium salts from hypervalent precursors proceed under acidic conditions. Ref. [44] describes the formation of $[(CF_3)_2I]Y$ from CF_3IX_2 ($X = F, Cl, OC(O)CF_3$) and $(CF_3)_2Cd\cdot D$ (D = donor) as well under basic conditions (MeCN, pyridine) as under acidic conditions ($B(OC(O)CF_3)_3$ in CH_2Cl_2 or SO_2). The identification of $[(CF_3)_2I]Y$ by ^{19}F NMR in the product mixtures was not unambiguous [44]. The reaction of $(CF_3)_2CFI$ with ClOX ($X = ClO_3, SO_2F$) gave solids (Eq. (44)) whereas the unbranched perfluoroalkyl iodides were converted into the corresponding ethers R_FOX (colorless liquids). Christe et al. proposed an ionic constitution of the solid products from the Raman spectroscopic comparison with $M[I(OX)_4]$ salts [32,33]

$$2(CF_3)_2CFI + 2ClOX \xrightarrow{autoclave} [((CF_3)_2CF)_2I][I(OX)_4] \tag{44}$$

where $X = ClO_3$ (-196 to $-45\,^\circ C$, several days), SO_2F (-45 to $20\,^\circ C$).

2.1.4. *Perfluoroalkyliodate anions $[(R_F)_nIX_{4-n}]^-$*

In the literature we have found only two examples of anions with perfluoroalkyl groups, namely *cis*-$[(CF_3)_2IF_2]^-$ [44] and $[CF_3ICl_3]^-$ [70].

cis-$[(CF_3)_2IF_2]^-$ was assigned from the ^{19}F NMR spectrum in the reaction mixture of CF_3IF_2 and $Hg(CF_3)_2$ in the weakly coordinating solvent CH_2Cl_2 (Eq. (45)). The $[CF_3ICl_3]^-$ anion was formed from CF_3ICl_2 and Cl^- and was stabilised in the presence of the weakly polarising cation $[Ph_4As]^+$ (Eq. (46))

$$CF_3IF_2 + Hg(CF_3)_2 \xrightarrow{CH_2Cl_2, -30\,^\circ C} cis\text{-}[(CF_3)_2IF_2]^- + (CF_3)_2IF + \ldots \tag{45}$$

$$CF_3ICl_2 + Ph_4AsCl \xrightarrow{CH_2Cl_2 -78\,^\circ C} [Ph_4As][CF_3ICl_3]. \tag{46}$$

2.2. *Per- and polyfluoroorganoiodine(V) compounds*

2.2.1. *Per- and polyfluoroorganoiodine(V) molecules, R_FIF_4*

Two pathways to per- and polyfluoroorganoiodine(V) compounds are known: the oxidative route which starts from mono or trivalent per- and polyfluoroorganoiodine compounds and the nucleophilic introduction of the organo group into the inorganic iodine(V) parent compound, IF_5. No example of a disproportionation of R_FIX_2 into R_FIX_4 and R_FI in analogy to the disproportionation of IF_3 has been reported as a preparative route so far.

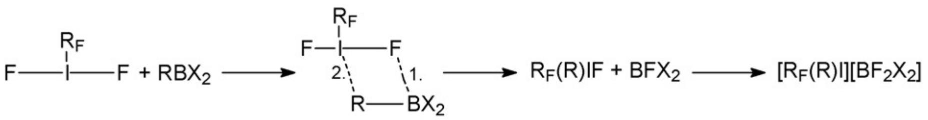
In order to reach I(V) it is obvious that (a) the fluorinating agent must be stronger and (b) the fluorinating conditions must be more severe than for I(III). Consequently, oxidative cleavage of the C–I bond and in case of unsaturated organo groups fluorine addition across double bonds are concurring reactions. The addition of F_2 to one of the two lone pairs of electrons at iodine in R_FIF_2 is in principle possible in inert solvents like CCl_3F. R_FIF_2, which is formed by the addition of F_2 to R_FI at $-78\,^\circ C$, is insoluble at this temperature. At $-40\,^\circ C$ R_FIF_2 becomes soluble in trace amounts which react fast with F_2 (Eqs. (47a) and (47b)) or undergo by-reactions. Generally, the direct fluorination is not a favoured route to R_FIF_4

$$R_FI \xrightarrow[CCl_3F, -78\,^\circ C]{F_2-N_2(\leq 10\%)} R_FIF_2 \xrightarrow[CCl_3F, -40\,^\circ C]{F_2-N_2(<10\%)} R_FIF_4 \tag{47a}$$

$$R_FI \xrightarrow[CCl_3F, -40\,^\circ C]{F_2-N_2(\leq 10\%)} R_FIF_4 \tag{47b}$$

where $R_F = CF_3$ [4].

The fluorination of monovalent R_FI to R_FIF_4 with ClF_3 (Eq. (48)) is a delicate reaction, which often ends with mixtures of I(III and V)



Scheme 1. The interaction between R_FIF_2 and RBX_2 and the introduction of group R into the iodine moiety.

products. In case of C_6F_5I addition across C=C double bonds has to be mentioned as one side-reaction

$$3R_FI + 4ClF_3 \rightarrow 3R_FIF_4 + 2Cl_2 \tag{48}$$

where $R_FI = C_nF_{2n+1}$ (n = 1, 2, 3, 4, 6, 10) [6,71,72] $SF_5(CF_2)_nI$ (n = 2, 4) [73] C_6F_5I, 1,4-$C_6F_4I_2$ [74].

Excess of BrF_3 or BrF_5 is proposed for obtaining R_FIF_4 compounds (BrF_3 [6,24], BrF_5 ($R_F = C_2F_5$, C_4F_9, C_6F_{13} [6,24], C_6F_5 [10])). C_6F_5I adds fluorine in a slow reaction with $C_6F_5BrF_2$ or $C_6F_5BrF_4$ and forms $C_6F_5IF_4$ besides to $C_6F_5IF_2$.

The addition of fluorine to R_FI or R_FIF_2 using XeF_2 is likewise a slow reaction [17] and can be accelerated by catalytic amounts of weak Lewis acids (Eq. (49)). The influence of stronger Lewis acids will be discussed below. The reaction of C_6F_5I with XeF_2 in aHF in the presence of equimolar amounts of water gives mixtures of $C_6F_5IF_2$ and $C_6F_5IF_4$ [20]

$$R_FI \xrightarrow[\leq 40\,^\circ C]{XeF_2} R_FIF_2 \xrightarrow[\leq 65\,^\circ C]{XeF_2} R_FIF_4 \tag{49}$$

where $R_F = C_6F_5$ [17], 2,3,5,6-C_5F_4N [75].

Only one example describes the oxidative addition of fluorine to R_FIF_2 using a derivative of positive chlorine (Eq. (50)). This reaction reveals an interesting aspect. The first step is the addition of Cl(I) followed by $[OCF_3]^-$ or F^-. The intermediate $CF_3I(Cl)F_2Y$ (Y = OCF_3 or F) contains a negatively polarised chlorine bonded at I(V). Generally, Cl^- acts as reducing agent for I(V). In this case the consecutive reaction of $Cl^{\delta-}$ with $^{\delta+}ClOCF_3$ must be faster than the internal redox reaction and ends with CF_3IF_4 [76]

$$CF_3IF_2 + 2ClOCF_3 \xrightarrow[-30\,^\circ C]{\text{no solv.}} CF_3IF_4 + Cl_2 + 2C(O)F_2 \tag{50}$$

XeF_2 in the presence of medium to strong Lewis acids takes over the oxidiser property of $[FXe]^+$. Thus, reactions with $C_6F_5IF_2$ and C_6F_5I show two reaction channels: (a) fluorine addition to I(III) or I(I) and (b) across the C=C double bond (Eqs. (51a) and (51b)) [77]

$$\begin{aligned} &C_6F_5IF_2 + 5XeF_2 \xrightarrow{CF_3CH_2CF_2CH_3,\,20\,^\circ C\,[BF_3]} 1,4\text{-}C_6F_7IF_4 + C_6F_9IF_4 \\ &\quad + \ldots \end{aligned} \tag{51a}$$

$$C_6F_5I + 4XeF_2 \xrightarrow{aHF,\,20\,^\circ C\,[NbF_5]} C_6F_9IF_4 + \ldots \tag{51b}$$

In the acid-catalysed fluorine addition, the C=C double bond, at which iodine(I or III) is attached, is strongly polarised and undergoes no fluorine addition. This makes the procedure also suitable for the preparation of alk-1-en-1-yl-iodine tetrafluorides, exemplified for *cis*- and *trans*-$(CF_3)_2CFCF{=}CFIF_4$ [77]. Even perfluoroalkyl iodides can be fluorinated to alkyliodine tetrafluorides using the combination XeF_2/Lewis acid [77].

Preferable reactions to synthesise $C_6F_5IF_4$ are based on the nucleophilic substitution of one fluorine in IF_5 by C_6F_5. Efficient aryl transfer reagents are $C_6F_5SiF_3$ (Eq. (52a)) [78], $[NMe_4][C_6F_5SiF_4]$ (Eq. (52b)) [79], and $Bi(R_F)_3$ (Eq. (53)) [80]

$$IF_5 + C_6F_5SiF_3 \xrightarrow{MeCN,\,82\,^\circ C} C_6F_5IF_4 + SiF_4 \tag{52a}$$

$$IF_5 + [NMe_4][C_6F_5SiF_4] \xrightarrow{CH_2Cl_2,\,\leq 20\,^\circ C} C_6F_5IF_4 + [NMe_4][SiF_5] \tag{52b}$$

$$3IF_5 + Bi(R_F)_3 \xrightarrow{MeCN,\,82\,^\circ C} 3R_FIF_4 + BiF_3\downarrow \tag{53}$$

Besides $C_6F_5IF_4$ [78,80,82], 2,6-$C_6H_3F_2IF_4$ [81] 2,3,5,6-$C_5F_4NIF_4$ [75], and CF_3IF_4 [82] were obtained using $Bi(R_F)_3$ reagents.

The $[C_6F_5SiF_4]^-$ anion is a good source of the C_6F_5 nucleophile. IF_5 reacted fast with $[NMe_4][C_6F_5SiF_4]$ in CH_2Cl_2 and formed $C_6F_5IF_4$ besides $[SiF_5]^-$ (Eq. (52b)).

An alternative route, the electrophilic attack of $[IF_4]^+$ on C_6F_5H or 1,3,5-$C_6H_3F_3$, is given in the following equation [83]

$$Ar_F\text{-}H + [IF_4][SbF_{6-n}Cl_n] \xrightarrow{aHF,\,SO_2ClF \text{ or } IF_5} ArFIF_4 + \langle H[SbF_{6-n}Cl_n]\rangle \tag{54}$$

where $Ar_F = C_6F_5$, 1,3,5-$C_6F_3H_3$.

2.2.2. *Per- and polyfluoroorganoiodonium(V) salts $[R_F(R')IF_2]Y$*

$[R_FR'IF_2]Y$ salts with one or two C_6F_5 groups are the result of actual research. Starting from $C_6F_5IF_4$ one fluorine of the 5c-8e hypervalent IF_4 group can be substituted by an aryl group Ar (Ar = C_6F_5, FC_6H_4) (Eq. (55)) [26]. (Eq. (55)) demonstrates how widely applicable reagents fluoroorganodifluoroboranes are in polyvalent halogen chemistry for the introduction of fluoroorgano groups

$$C_6F_5IF_4 + ArBF_2 \xrightarrow{CH_2Cl_2,\,20\,^\circ C} [C_6F_5(Ar)IF_2][BF_4] \tag{55}$$

where Ar = C_6F_5, 2-FC_6H_4, 3-FC_6H_4, 4-FC_6H_4.

2.3. *Perfluoroorganobromine(III) compounds*

2.3.1. *Perfluoroorganobromine(III) molecules, R_FBrF_2*

Only three publications deal with the synthesis of perfluoroarylbromine(III) molecules. $C_6F_5BrF_2$ was claimed as a product of the addition of fluorine to R_FBr [84], but the published characteristic properties and spectroscopic data contradict the unambiguous characterisation given for the fluorine/C_6F_5 substitution products on BrF_3 (Eq. (56)) [85]

$$BrF_3 + C_6F_5SiF_3 \xrightarrow{CCl_3F,\,-5\,^\circ C} C_6F_5BrF_2 + SiF_4 \tag{56}$$

$(C_6F_5)_2M$ reagents with a weak acidic metal centre and the effective nucleophilic C_6F_5 group are able to substitute one fluorine in BrF_3 (Eq. (57)) [86].

With an excess of $(C_6F_5)_2M$ reagents it was not possible to introduce a second C_6F_5 group and to form neither $(C_6F_5)_2BrF$ nor the cation $[(C_6F_5)_2Br]^+$ (Eq. (58)) [86]

$$2BrF_3 + (C_6F_5)_2M \xrightarrow{MeCN,\,\leq 0\,^\circ C} 2C_6F_5BrF_2 + MF_2\downarrow \tag{57}$$

where M = Zn, Cd, Hg [86]

$$\begin{aligned} &2C_6F_5BrF_2 \\ &\quad + (C_6F_5)_2Cd \xrightarrow{MeCN,\,\leq 0\,^\circ C} \text{neither}(C_6F_5)BrF \text{ nor } [(C_6F_5)_2Br]^+. \end{aligned} \tag{58}$$

2.3.2. *Perfluoroorganobromonium salts $[R_F(R')Br]Y$*

Bis(pentafluorophenyl)bromonium salts, $[(C_6F_5)_2Br]Y$ (Y = BF_4, AsF_6, SbF_6, PF_6), represent the majority of bromonium compounds which contain perfluorinated organic groups bonded to Br(III). The routes elaborated for the syntheses of non-fluorinated or mono-fluorinated organobromonium salts were unsuccessful for their polyfluorinated analogues $[R_F(R')Br]Y$. For instance, the electrophilic alkylation of organyl bromides RBr with CH_3F–SbF_5 in SO_2 gave methylbromonium salts $[CH_3(R)Br][SbF_6]$ in good yields (R = alkyl, alkenyl, and aryl), but failed for R = 4-C_6BrF_4 [51]. The pentafluorophenylation of C_6F_5Br with molten $[C_6F_5Xe][AsF_6]$ resulted in $[(C_6F_5)_2Br][AsF_6]$, but in a very low yield (Eq. (59)) [40]

$$\begin{aligned} &C_6F_5Br(\text{excess}) \\ &\quad + [C_6F_5Xe][AsF_6] \xrightarrow[\text{melt},\,1\text{ h}]{140\,^\circ C} \underset{6\%}{[(C_6F_5)_2Br][AsF_6]} + \underset{83\%}{C_6F_6} + Xe^0 \end{aligned} \tag{59}$$

The arylation of BrF_3 with $(XC_6H_4)_4Sn$ [87] or $(XC_6H_4)_2Hg$ [88] led to the salts $[Ar_2Br][BF_4]$ in high yields, but Nesmejanov et al.

reported that $(C_6F_5)_4Sn$ and $(C_6F_5)_2Hg$ were not reactive or underwent oxidative fluorination across the C=C bond [87,88]. Few years ago, a convenient route to $[(C_6F_5)_2Br]Y$ was elaborated by Frohn et al. Pentafluorophenyl groups were introduced into BrF_3 using the corresponding organoborane or the combination cadmiumorganyl-Lewis acid (Eqs. (60) and (61)) [86]

$$BrF_3 + (C_6F_5)_2BF \xrightarrow[-78\ \text{to}\ 20\,^\circ\text{C},1\ \text{h}]{CH_2Cl_2/<MeCN} \underset{93\%}{[(C_6F_5)_2Br][BF_4]} \quad (60)$$

$$C_6F_5BrF_2 + 0.5Cd(C_6F_5)_2 + BF_3\cdot NCMe \xrightarrow[-78\ \text{to}\ 20\,^\circ\text{C}]{CH_2Cl_2/<MeCN} \underset{20\text{–}30\%}{[(C_6F_5)_2Br][BF_4]} \quad (61)$$

The use of $AsF_5{\cdot}NCMe$ or $SbF_5{\cdot}NCMe$ instead of $BF_3{\cdot}NCMe$ (Eq. (61)) gave the corresponding hexafluoroarsenate and hexafluoroantimonate in the same yield. However, better yields of $[(C_6F_5)_2Br][AsF_6]$ and $[(C_6F_5)_2Br][SbF_6]$ were obtained by treating the tetrafluoroborate salt with AsF_5 in CH_2Cl_2 or with SbF_5 in SO_2 [86]. Effective carbon nucleophiles can be introduced into the bromine environment using the perfluoroorganodifluoroborane route, discussed above (Eq. (39d) and Scheme 1) and exemplified by (Eq. (62)) [89]

$$C_6F_5BrF_2 + C_3F_7C{\equiv}CBF_2 \xrightarrow[-40\ \text{to}\ 0\,^\circ\text{C}]{PFP} [C_3F_7C{\equiv}C(C_6F_5)Br][BF_4] \quad (62)$$

where PFP = $CF_3CH_2CHF_2$.

2.4. *Perfluoroorganobromine(V) molecules, R_FBrF_4 and R_FBrO_2*

Three perfluoroorganobromine tetrafluorides are reported in the literature resulting from fluorine addition to the corresponding monovalent perfluoroorganyl bromides, $C_6F_5BrF_4$ [90], $C_3F_7BrF_4$ [91], and $C_7F_{15}BrF_4$ [92]. The independent synthesis of $C_6F_5BrF_4$ by fluorine/C_6F_5 substitution (Eq. (63)) [93] showed that the preceding report [90] was erroneous. Consequently, missing of an unambiguous proof for $C_3F_7BrF_4$ and $C_7F_{15}BrF_4$ calls the reported data into question [91,92]. Winfield et al. showed that the attempted fluorine addition to bromine in C_6F_5Br with ClF_3 ended neither with $C_6F_5BrF_2$ nor $C_6F_5BrF_4$ [74]. Fluorine was only added across the C=C double bonds of the aryl group. Frohn et al. offered four procedures to introduce the C_6F_5 group into the Br(V) moiety. In Eqs. (63)–(65) and (67) BrF_5 or $K[BrF_6]$ were used as starting materials and $C_6F_5SiF_3$, $(C_6F_5)_nSiMe_{4-n}$ (n = 1, 2), or $M(C_6F_5)_2$ (M = Zn, Cd) as reagents of different acidity [93,94]. They also showed that BrO_2F underwent fluorine/pentafluorophenyl substitution and formed $C_6F_5BrO_2$ (Eq. (68)) [95]

$$BrF_5 + C_6F_5SiF_3 \xrightarrow[[2MeCN]]{C_2Cl_2F_4,0\,^\circ C} C_6F_5BrF_4 + SiF_4\ [93] \quad (63)$$

$$2K[BrF_6] + C_6F_5SiF_3 \xrightarrow{MeCN,-40\,^\circ C} C_6F_5BrF_4 + K_2[SiF_6] + BrF_5\ [96] \quad (64)$$

$$BrF_5 + \tfrac{1}{n}(C_6F_5)_nSiMe_{4-n} \xrightarrow[[2MeCN]]{CH_2Cl_2,\,0\,^\circ C} C_6F_5BrF_4 + \tfrac{1}{n}Me_{4-n}SiF_n[94] \quad (65)$$

where n = 1, 2, but

$$K[BrF_6] + C_6F_5SiMe_3 \rightarrow K[BrF_4] + C_6F_6 + Me_3SiF\ [96] \quad (66)$$

$$BrF_5 + 0.5M(C_6F_5)_2 \xrightarrow{CH_2Cl_2,0\,^\circ C} C_6F_5BrF_4 + 0.5MF_2\downarrow\ [94] \quad (67)$$

where M = Zn, Cd.

$$2BrO_2F + (C_6F_5)_2Cd \xrightarrow{MeCN,-25\,^\circ C} 2C_6F_5BrO_2 + CdF_2\downarrow\ [95]. \quad (68)$$

2.5. *Perfluoroarylchlorine(III and V) molecules*

Two references dealing with perfluoroorganochlorine(III) compound can be found in literature. The syntheses claimed for $C_6F_5ClF_2$ [97] and $C_6F_5Cl(F)Cl(F)C_6F_5$ [98] were performed as fluorine additions to C_6F_5Cl in analogy to the erroneous report on the synthesis of $C_6F_5BrF_2$ and $C_6F_5BrF_4$ (autoclave, 117 °C). There is no comprehensible proof for the two molecules.

3. Typical transformations on polyvalent perfluoroorganohalogen(III and V) compounds and important reactivities of the halogen centers

The first part of this chapter deals with transformations of the $HalX_2$ and $HalX_4$ unit in perfluoroorganohalogen(III and V) molecules and concentrates on transformations of IF_2 or IF_4, $I(acyloxy)_2$, and IO or IO_2 groups. The very polar I–F bond reacts with weakly Lewis acidic reagents like silanes R_3SiY according to (Eq. (69)) to the corresponding R_FIY_2 molecules

$$R_FIF_2 + 2R_3EY \rightarrow R_FIY_2 + 2R_3EF \quad (69)$$

where E = Si, R = Me, R_F = CF_3: Y = OMe [99]; E = Si, R = Me, R_F = CF_3: Y = Cl [70]; E = Si, R = Me, R_F = C_6F_5: Y = CN [100].

The specific substitution of only one fluorine of the IF_2 triad using Me_3SiOMe for example seems not possible. But starting from the asymmetric triad Cl–I–F, the specific substitution of fluorine could be realised (Eq. (70)) [99]

$$CF_3I(Cl)F + Me_3SiOMe \rightarrow CF_3I(Cl)OMe + Me_3SiF \quad (70)$$

A related transformation was used to obtain a rare example of R_FICl_2 molecules (Eq. (71)) [102]

$$CF_3I(Cl)F + Me_3SiCl \rightarrow CF_3ICl_2 + Me_3SiF \quad (71)$$

Even BY_3 (Y = Cl, Br, I, $OC(O)CF_3$) and Me_3SiCN were claimed as reagents to obtain the corresponding molecules CF_3IY_2 and $CF_3I(CN)_2$ [70].

With boranes RBX_2 of different acidity, carbon nucleophiles could be introduced under formation of numerous iodonium(III) salts (Eq. (72)), see Section 2.1.3

$$R_FIF_2 + RBX_2 \rightarrow [R_F(R)I][BF_2X_2] \quad (72)$$

In addition to Si- and B-electrophiles also carbon electrophiles like $(CF_3C(O))_2O$ were applied in the acid-assisted substitution of F against a O-nucleophile, here $OC(O)CF_3$ (Eqs. (73a) and (73b)). The same strategy can be used to introduce other oxoacid anions as demonstrated in the case of ONO_2 (Eq. (74))

$$R_FIF_2 + 2(CF_3C(O))_2O \rightarrow R_FI(OC(O)CF_3)_2 + 2CF_3C(O)F \quad (73a)$$

where R_F = CF_3 [103], C_6F_5 [11]

$$C_6F_5BrF_2 + 2(CF_3C(O))_2O \rightarrow C_6F_5Br(OC(O)CF_3)_2 + 2CF_3C(O)F[85,104] \quad (73b)$$

$$R_FIF_2 + 3N_2O_5 \rightarrow R_FI(F)ONO_2 + R_FI(ONO_2)_2 + 3NO_2F \quad (74)$$

where R_F = CF_3 [30], C_6F_5 [9].

Transformations of $I(OC(O)CF_3)_2$ groups are dominated by the substitution of one acyloxy group by an aryl group under proton assistance (electrophilic introduction of the $R_FI(OC(O)CF_3)$

unit into benzene derivatives) (Eq. (75)), for more details see Section 2.1.3

$$R_FI(OC(O)CF_3)_2 + C_6H_5Me \xrightarrow{[H^+]} [R_F(C_6H_4Me)I][OC(O)CF_3] + CF_3C(O)OH \qquad (75)$$

where $R_F = C_3F_7$, C_6F_{13}, C_6F_5 [55].

A related reaction for the introduction of activated benzene derivatives into the perfluoroalkyliodine(III) moiety is given in (Eq. (76)) [105]

$$C_nF_{2n+1}IO + 1,4\text{-}C_6H_4(SiMe_3)_2 \xrightarrow{Me_3SiOTf} [C_nF_{2n+1}(4\text{-}Me_3SiC_6H_4)I][OTf] \qquad (76)$$

The synthesis of hydroxy(tosyloxy)iodoperfluoroalkanes has to be mentioned (Eq. (77)), because this class of compounds makes useful reagents available [106]

$$R_FI(OC(O)CF_3)_2 + TsOH \cdot H_2O \rightarrow R_FI(OH)OTs \qquad (77)$$

In principle R_FIX_2 and R_FIX_4 molecules can be transformed into the corresponding oxo derivatives R_FIO (C_6F_5IO [12,36,40,105]; CF_3IO [35]), R_FIOF_2 (CF_3IOF_2 [35], $C_6F_5IOF_2$ [107]), and R_FIO_2 (CF_3IO_2 [35], $C_6F_5IO_2$ [107]. In aqueous media, this conversion can be considered as an equilibrium reaction with acidic HX as co-product. Therefore, an excess of alkaline media is necessary. Under the influence of OH^- the product can undergo subsequent reactions. One indicator may be the strongly differing physical data, e.g. the temperature of decomposition [36,39], solubilities [49,108,109], and IR spectroscopic data [36,40] reported for C_6F_5IO together with the spectroscopically proofed presence of $[(C_6F_5)_2I][IO_3]$ [40]. $IO_3{}^-$ anions may be the result of the pronounced nucleofugality of the C_6F_5 group in $[C_6F_5(OH)IO]^-$ as an intermediate in the presence of OH^-. Thus in 1 M $NaOH_{aq}$ at 100 °C the C–I bond is cleaved and C_6F_5H is formed quantitatively within 3 h [40]. The formation of CF_3IO is described by (Eq. (78)). This path has strong similarity to (Eq. (69)). CF_3IO is intrinsically unstable. In contrast to C_6F_5IO its disproportion to CF_3I and CF_3IO_2 is described [35]. CF_3IO can be acylated with $(CF_3C(O))_2O$ to give $CF_3I(OC(O)CF_3)_2$ [103]

$$2CF_3IF_2 + SiO_2 \xrightarrow[-40\,^\circ C]{MeCN} 2CF_3IO + SiF_4 \qquad (78)$$

$C_6F_5IOF_2$ and $C_6F_5IO_2$ can be obtained from the homogenous reaction system of $C_6F_5IF_4$ and $(Me_3Si)_2O$ in the basic solvent MeCN (Eqs. (79a) and (79b)). The presence of MeCN is essential, because it solvates the intermediate $C_6F_5IOF_2$. In polar, weakly coordinating solvents like CH_2Cl_2 mixtures of products result only

$$C_6F_5IF_4 + (Me_3Si)_2O \xrightarrow{MeCN} C_6F_5IOF_2 + 2Me_3SiF \qquad (79a)$$

$$C_6F_5IOF_2 + (Me_3Si)_2O \xrightarrow{MeCN} C_6F_5IO_2 + 2Me_3SiF \qquad (79b)$$

CF_3IOF_2 was obtained from the reaction of CF_3IF_4 and SiO_2 and showed an unexpected reactivity in the presence of Lewis acids, the elimination of CF_4 (Eq. (80)) [110]

$$CF_3IOF_2 + BF_3 \rightarrow CF_4 + [IO][BF_4] \qquad (80)$$

In contrast to $C_6F_5IF_2$ the hydrolysis of $C_6F_5BrF_2$ in aqueous medium did not end with unsoluble C_6F_5BrO but with C_6F_5Br and O_2. In a fast internal redox reaction O^{-II} was oxidised by Br(III) (Eq. (81)). The hydrolysis of $C_6F_5BrF_4$ differs in principle from that of $C_6F_5IF_4$ and $C_6F_5BrF_2$. Thus, hydrolysis did not result in an insoluble, polymeric dioxide, but in water-soluble $C_6F_5BrO_2$. The latter was also isolated from the reaction of $C_6F_5BrF_4$ with $(Me_3)_2SiO$ (Eqs. (82a) and (82b)) as an explosive (<20 °C) solid which was characterised by the iodometric oxidation equivalent and by ^{19}F and ^{13}C NMR and IR spectroscopy [95]. The equimolar reaction of $C_6F_5BrF_4$ and $(Me_3Si)_2O$ in MeCN did not result in $C_6F_5BrOF_2$ (Eq. (83)) [95]. $C_6F_5BrOF_2$ was obtained from $C_6F_5BrF_4$ and $CsNO_3$ (Eq. (84)) [95]

$$2C_6F_5BrF_2 + 2H_2O \xrightarrow{MeCN} 2C_6F_5Br + O_2 + 4\,HF \qquad (81)$$

$$C_6F_5BrF_4 + 2H_2O \xrightarrow{MeCN} C_6F_5BrO_2 + 4HF \qquad (82a)$$

$$C_6F_5BrF_4 + 2(Me_3Si)_2O \xrightarrow{MeCN} C_6F_5BrO_2 + 4Me_3SiF \qquad (82b)$$

$$2C_6F_5BrF_4 + 2(Me_3Si)_2O \xrightarrow{MeCN} \overset{\text{no } C_6F_5BrOF_2!}{C_6F_5BrF_4 + C_6F_5BrO_2 + 4Me_3SiF} \qquad (83)$$

$$C_6F_5BrF_4 + CsNO_3 \xrightarrow{MeCN} C_6F_5BrOF_2 + NO_2F + CsF \qquad (84)$$

Double bonded oxygen in R_FIO could be substituted by two oxoacid anions (Eqs. (85a)–(85c)) in reactions with oxoacid anhydrides ($(CF_3C(O))_2O$ [103], N_2O_5 [9,30], Cl_2O [14]) or by two fluorine atoms with SF_4 (Eq. (86a)) [12,111]. Substitution of oxygen by fluorine with SF_4 is also possible starting with $R_FI(OC(O)CF_3)_2$ directly (Eq. (86b)) [12,111]

$$R_FIO + (CF_3C(O))_2O \rightarrow R_FI(OC(O)CF_3)_2 \qquad (85a)$$

where $R_F = CF_3$.

$$R_FIO + N_2O_5 \rightarrow R_FI(ONO_2)_2 \qquad (85b)$$

$$R_FIO + Cl_2O \rightarrow R_FI(OCl)_2 \qquad (85c)$$

$$R_FIO + \geq 1SF_4 \rightarrow R_FIF_2 + SOF_2 \qquad (86a)$$

where $R_F = C_3F_7$, C_6F_5.

$$R_FI(OC(O)CF_3)_2 + \geq 2SF_4 \rightarrow R_FIF_2 + 2SOF_2 + 2CF_3C(O)F \qquad (86b)$$

where $R_F = C_3F_7$.

The Hal(III and V)F_n groups in $C_6F_5HalF_n$ (n = 2, 4) are amphoteric. Until now, their Lewis acidic properties were predominantly investigated. Thus, 1:1 adducts of $C_6F_5IF_2$ and bidentate (2,2′-bipyridyl, 1,10-phenathroline) and monodentate (quinoline) N-bases were isolated and structurally characterised (Eq. (87a)) [101]. $C_6F_5BrF_4$ forms a 1:1 adduct with pyridine (Eq. (88)) which is more stable than $BrF_5{\cdot}py$ and decomposes only at 124.5 °C [96]. The hard fluoride base (CsF in MeCN at 0 °C) initiates elimination of C_6F_6 (Eq. (89)). This interaction is accompanied by reduction of Br(V) under $[BrF_4]^-$ formation [96]

$$C_6F_5IF_2 + \text{N-base} \rightarrow C_6F_5IF_2{\cdot}\text{N-base} \qquad (87a)$$

where N-base = 2,2′-bipyridyl, 1,10-phenathroline, quinoline.

$$CF_3IF_2 + \text{N-base} \rightarrow CF_3IF_2{\cdot}\text{N-base} \qquad (87b)$$

where N-base = MeCN, py, quinoline [112].

$$C_6F_5BrF_4 + py \rightarrow C_6F_5BrF_4{\cdot}py \qquad (88)$$

$$C_6F_5BrF_4 + CsF \xrightarrow{MeCN, 0\,^\circ C} C_6F_6 + Cs[BrF_4] \qquad (89)$$

Only little is known about organo(fluoro)halonium salts. Perfluoroalkyliodine difluorides react with BF_3 in CH_2Cl_2 at −60 °C and form a precipitate of unknown composition [47]. Perfluoroorganyliodine tetrafluorides R_FIF_4 ($R_F = C_6F_{13}$, $(CF_3)_2CFCF{=}CF$, *cyclo*-C_6F_9, C_6F_5) resist to Lewis acids like aHF, NbF_5 in aHF, and BF_3 in PFB (20–22 °C) for some hours [77], but perfluoroalkyliodine tetrafluorides react with AsF_5 (−78 °C) [71] and perfluoroalkyliodine oxydifluorides with BF_3 (−78 °C), AsF_5

(−20 °C) or SbF_5 (0 °C) [110]. These reactions are accompanied by the decomposition of the polyvalent iodo compounds under formation of the corresponding perfluoroalkanes. Fluoride abstraction from $C_6F_5IF_4$ with SbF_5 in SO_2FCl at low temperatures and formation of $[C_6F_5IF_3]^+$ was proved by ^{19}F NMR spectroscopy [83]. Higher stability is found when two aryl groups are present in the arylfluoroiodonium(V) cation. The synthesis and structure [25,113] of $[(C_6F_5)(Ar)IF_2][BF_4]$ is discussed in Sections 2.2.2 and 6.

A few examples of chemical transformations of perfluoroorganyl groups bonded to Hal centres were reported, e.g. the electrophilic oxygenation [114] and fluorine addition [77] to the C_6F_5 group in $C_6F_5IF_n$ (n = 0, 2, 4) (Eqs. (90a) and (90b))

$$C_6F_5IF_4 + XeF_2 + H_2O \xrightarrow[-Xe]{HF,\,12\,^\circ C} \textit{cyclo}\text{-}3\text{-}O\text{-}C_6F_5IF_4(\text{main product}) \tag{90a}$$

$$C_6F_5IF_4 + XeF_2 \xrightarrow[-Xe]{HF,[NbF_5]\,20\,^\circ C} \textit{cyclo}\text{-}C_6F_9IF_4 \tag{90b}$$

Perfluoroorganohalogen fluorides are interesting fluorinating agents (Eq. (91) [93], Eqs. (92a) and (92b)) [10] which have certain advantages over halogen fluorides itself taking into consideration the inertness of the by-product, R_FHal, relative to Hal_2 formed from halogen fluorides

$$2R_3P + C_6F_5BrF_4 \rightarrow 2R_3PF_2 + C_6F_5Br \tag{91}$$

$$C_6F_5I + 2C_6F_5BrF_2 \xrightarrow{MeCN} C_6F_5IF_2 + C_6F_5Br + < 1C_6F_5IF_4 \tag{92a}$$

$$2C_6F_5I + C_6F_5BrF_4 \xrightarrow[MeCN,-30\,^\circ C]{[BF_3\cdot MeCN]} 2C_6F_5IF_2 + C_6F_5Br \tag{92b}$$

The slow addition of fluorine across the C=C double bond of hexafluoropropene with CF_3IF_4 (Eq. (93)) was reported [71]

$$CF_3IF_4 + CF_3CF{=}CF_2 \xrightarrow[20\,^\circ C,2\,d]{} (CF_3)_2CFI + \ldots \tag{93}$$

The cation, $[(C_6F_5)_2IF_2]^+$, is a significant stronger oxidiser and fluorinating agent than the molecules, $C_6F_5IF_4$ or IF_5. Thus, $[(C_6F_5)_2IF_2]^+$ affords fluorination of very weak reducing molecules like $(C_6F_5)_3Bi$ (Eq. (94)). Partially positively charged iodine in C_6F_5I was fluorinated, even in the presence of the basic solvent MeCN, which principally reduces the oxidation potential by coordination and charge transfer (Eq. (95)) [26]

$$[(C_6F_5)_2IF_2][BF_4] + (C_6F_5)_3E \xrightarrow{MeCN} [(C_6F_5)_2I][BF_4] + (C_6F_5)_3EF_2 \tag{94}$$

where E = P, As, Sb, Bi

$$[(C_6F_5)_2IF_2][BF_4] + C_6F_5I \xrightarrow{MeCN} [(C_6F_5)_2I][BF_4] + C_6F_5IF_2. \tag{95}$$

4. Polyvalent perfluoroorganoiodine compounds: applications and reagents in synthetic chemistry

Because of their electrophilic character, neutral R_FIX_n (n = 2, 4) and cationic $[R_F(R')I]^+$ are predestined for the electrophilic transfer of perfluoroorganyl groups on nucleophiles. Especially the perfluoroalkylation of different kinds of nucleophiles was developed by Yagupol'skii and intensively investigated by Umemoto. Only few examples of different kinds of nucleophiles demonstrate the potential of perfluoroalkyl(phenyl)iodonium cations. The favoured formation of iodobenzene as a nucleofuge is a typical pattern of these perfluoroalkylation reactions (Eqs. (96)–(101)) [115–119]

$$[C_6F_{13}(C_6H_5)I][BF_4] + Me_2S \xrightarrow[-C_6H_5I]{} [C_6F_{13}SMe_2][BF_4]\ [115] \tag{96}$$

$$[C_6F_{13}(C_6H_5)I][BF_4] + 1,2\text{-}(RO)_2C_6H_4 \xrightarrow[-C_6H_5I]{Py} 4\text{-}C_6F_{13}\text{-}1,2\text{-}(RO)_2C_6H_3\ [116] \tag{97}$$

$$[C_6F_{13}(C_6H_5)I][BF_4] + (Me_2N)_3P \xrightarrow[-C_6H_5I]{} [C_6F_{13}P(NMe_2)_3][BF_4]\ [115] \tag{98}$$

$$[CF_3CH_2(C_6H_5)I][N(S(O)_2CF_3)_2 + \text{N-base} \xrightarrow[-C_6H_5I]{} CF_3CH_2\text{-N-alkylation}\ [117] \tag{99}$$

where N-base = imidazole and pyridine derivatives

$$[C_3F_7(C_6H_5)I]X + Me_3SnR \xrightarrow[-C_6H_5I]{} C_3F_7R + C_6H_5I + Me_3SnX\ [118] \tag{100}$$

where R = Ph, CH=CHPh, C≡CPh

$$[C_nF_{2n+1}(C_6H_5)I][OTf] + RMgX \xrightarrow[-C_6H_5I]{} C_nF_{2n+1}R + Mg(X,OTf)_2\ [119] \tag{101}$$

An interesting example of polyfluoroalkylation is the trifluoroethyl-*S*-alkylation of cysteine in water [120] (Eq. (102)) reported by DesMarteau et al.

$$[CF_3CH_2(C_6H_5)I][N(S(O)_2CF_3)_2] + HS\text{-}CH_2CH(NH_2)CO_2H \xrightarrow{H_2O} CF_3CH_2S\text{-}CH_2CH(NH_2)CO_2H \tag{102}$$

Recently, Togni et al. showed that 1-trifluoromethyl-1,3-dihydro-1,2-benziodoxoles [121], which can formally be regarded as internal perfluoroalkyl(aryl)iodonium salts, possess a remarkable potential as a mild electrophilic trifluoromethylation agent for carbon- and sulphur-centred nucleophiles [122].

Carbon nucleophiles can be coupled with R_FIF_2 as demonstrated in (Eq. (103))

$$R_FIF_2 + 2Me_3SiC{\equiv}CPh \rightarrow R_FI + PhC{\equiv}C{-}C{\equiv}CPh + 2Me_3SiF\ [123] \tag{103}$$

Gladysz et al. reported the application of long-chain $R_FI(O\text{-}C(O)CF_3)_2$ molecules for oxidation reactions on 1,4-hydroquinones in fluorous phase systems [124]. Rondesvedt described the application of perfluoroalkyliodine difluorides for the telomerisation of perfluoroalkyl iodides with tetrafluoroethylene (Eq. (104)) [23,24]

$$a\,C_6F_{13}IF_2 + b\,C_3F_7I + c\,CF_2{=}CF_2 \xrightarrow{78\,^\circ C,8.4\,bar} F(CF_2)_nI \tag{104}$$

where n = odd from 3 to 19.

Actually, a promising application of polyfluorinated alkyl(aryl)iodonium salts with the weakly nucleophilic $[N(S(O)_2CF_3)_2]^-$ anion was developed by Montanari and Kumar [125–127]. During the solid phase peptide synthesis the electrophilic iodonium cation acts as an N-capping reagent for deletion products. This procedure allows an easy separation of the desired peptide from its deletion products.

5. NMR spectroscopic characteristics of polyvalent perfluoroorganoiodine and bromine(III and V) compounds

^{13}C and in particular ^{19}F NMR spectroscopy are key tools for the characterisation of polyvalent per- and polyfluoroorganylhalogen compounds in solution. We present only important NMR spectroscopic properties of perfluoroorganylbromine(III, V) and perfluoroorganyliodine(III, V) compounds and their distinctions from their parent compounds, perfluoroorganyl bromides and iodides. For convenience, typical ^{13}C and ^{19}F NMR spectral data of selected perfluoroorganyl-bromine(III, V) and -iodine(III, V) derivatives were compiled in Table 1.

Solutions of R_FHalF_2 in weakly coordinating solvents (CCl_4, CCl_3F, CH_2Cl_2, PFB, or PFP) are characterised by ^{19}F shift values of their $HalF_2$ triad at −155 to −178 ppm (IF_2) and at −45 to −60 ppm (BrF_2). The related $HalF_4$ fluorine resonances in R_FHalF_4 occur significantly deshielded, located at −5 to −30 ppm (IF_4) and at 70–92 ppm (BrF_4; R_F = aryl). In basic solvents (CH_3CN, Py, ether, THF) the $HalF_n$ resonances shift by 1–5 ppm to lower frequencies, which reflects the donor-acceptor interaction of R_FHalF_n with the solvent. The IF_4 resonance in R_FIF_4 usually presents a multiplet with $^3J(IF_4,F)$ and $^4J(IF_4,F)$ couplings depending mainly on the nature of R_F and varying in magnitude of 2–17 and 15–40 Hz, respectively [10,77,80,129]. The BrF_4 resonance in $C_6F_5BrF_4$ has a triplet structure with $^4J(BrF_4,F^{2,6})$ = 29 Hz [93]. The ^{19}F signals of IF_2 and BrF_2 in $C_6F_nH_{5-n}HalF_2$ are reported as unresolved singlets. Similarly, no $J(IF_2,F)$ couplings were detected in the spectra of perfluoroalkenyliodine difluorides $(CF_3)_2CFCF{=}CFIF_2$ (*cis* and *trans*) [5] and 1-IF_2-*cyclo*-C_6F_7-1,4 [8]. The spectra of polyfluoroalkyliodine difluorides, $C_nF_{2n+1}(CH_2)_mIF_2$ (m = 0, 1), display splitted IF_2 signals with $^3J(IF_2,H)$ = 8–12 Hz and $^4J(IF_2,F)$ = 5 Hz [18]. Thus, the $^3J(IF_2,H)$ coupling is of the same magnitude as the $^3J(IF_2,F)$ coupling in comparable molecules. The ^{19}F NMR spectrum of $(CF_3)_2IF$ (complex reaction mixture) is reported as a doublet at −26.1 ppm (2 CF_3) and a septet at −131.5 ppm (IF) with $^3J(F,F)$ = 6 Hz (CH_2Cl_2, −33 °C) [44]. The IF resonance in isolated $(C_6F_5)_2IF$ appears significantly more deshielded (∼120 ppm) at −11.7 ppm (CH_2Cl_2, 35 °C) and both C_6F_5 groups are chemically equivalent with resonances at −124.2 ($F^{2,6}$), −147.6 (F^4), and −158.2 ppm ($F^{3,5}$).

The ^{19}F NMR spectra of perfluoroorgano groups R_F bonded to Br(III and V) or I(III and V) differ from that of their parent compounds R_FBr and R_FI, respectively (Table 1). In the series of perfluoroalkyliodine fluorides, $C_nF_{2n+1}CF_2IF_m$, the increase of m from 0 to 2 and 4 causes a strong shielding of the CF_2I fluorine atoms. The maximal effect was found for the trifluoromethyl derivatives, CF_3IF_m, with shieldings [130] of $\Delta\delta(F^1)$ −27 (m = 2) and −50 ppm (m = 4) [129], respectively. This effect diminishes with elongation of the perfluoroalkyl chain (n = 1, 2, 3 [6], 6 (Table 1) to $\Delta\delta(F^1)$ = −16 ppm (n = 6, m = 2) and $\Delta\delta(F^1)$ = −22 ppm (n = 5, m = 4). A similar shielding effect was observed in the spectra of perfluoroalkenyliodine fluorides, *trans*-$(CF_3)_2CFCF{=}CFIF_m$: $\Delta\delta(F^1)$ = −14 ppm (m = 2) and $\Delta\delta(F^1)$ = −20 ppm (m = 4). The *ortho*-fluorine atoms $F^{2,6}$ in the C_6F_5 group which are one bond more separated from the IF_m substituent in $C_6F_5IF_m$ than F^1 in the corresponding alkyl or alkenyl derivatives show smaller low frequency shifts: $\Delta\delta(F^{2,6})$ = −2 ppm (m = 2) and $\Delta\delta(F^{2,6})$ = −10 ppm (m = 4). In the series of $C_6F_5BrF_m$ molecules the effect of m is negligible. Additionally, the *para*-fluorine atom in all $C_6F_5HalF_m$ compounds (Hal = Br, I) are deshielded by 10–12 ppm with respect to the parent molecule, C_6F_5Hal.

The ^{19}F NMR spectra of the halonium salts, $[R_FR'(Hal)]Y$, display a remarkable dependence on the nature of both the solvent and the counteranion, Y^-, because of the electrophilic character of their cations. Solutions of their salts in aHF (superacid) are characterised by “rarely-solvated” cations and solvated (protonated) anions. As an approximation, halonium salt solutions in aHF can be treated as such of nearly “naked” di(organyl)halonium cations and a separated, solvated anion, whereas in good coordinating basic solvents (MeCN, ether, THF) strongly coordinated halonium cations are separated from less solvated anions. In weakly coordinating solvents (PFP, CH_2Cl_2, $CDCl_3$), as far as solubility is observed, ion pairing is possible. Thus, when superacidic aHF was

Table 1

NMR spectral data of selected perfluoroorganohalogen(III and V) compounds[a]

Compound	Solvent	$\delta(^{19}F)$ (ppm)	$\delta(^{13}C)$ (ppm)	Reference
C_6F_5Br	CD_2Cl_2	−132.7 (2F, F^{2,6}), −154.9 (1F, F^4), −160.9 (2F, F^{3,5})	96.8 (C^1), 147.5 (C^{2,6}), 140.3 (C^{3,5}), 143.1 (C^4)	[94]
$C_6F_5BrF_2$	CCl_3F	−133.2 (2F, F^{2,6}), −144.0 (1F, F^4), −156.8 (2F, F^{3,5}), −44.5 (2F, BrF_2)	119.4 (C^1), 143.8 (C^{2,6}), 139.1 (C^{3,5}), 146.5 (C^4)[b]	[85]
$C_6F_5BrF_4$	CD_2Cl_2	−133.3 (2F, F^{2,6}), −142.6 (1F, F^4), −157.3 (2F, F^{3,5}), 92.0 (4F, BrF_4)	151.9 (C^1), 143.3 (C^{2,6}), 139.6 (C^{3,5}), 146.5 (C^4)	[94]
$[(C_6F_5)_2Br][BF_4]$	CD_3CN	−129.3 (2F, F^{2,6}), −139.6 (1F, F^4), −155.2 (2F, F^{3,5})	102.6 (C^1), 146.1 (C^{2,6}), 139.5 (C^{3,5}), 147.7 (C^4)	[86]
$C_6F_{13}I$	CCl_3F	−59.6 (2F, F^1), −81.4 (3F, F^6), −113.6 (2F, F^2), −122.1 (2F, F^3), −123.5 (2F, F^4), −127.1 (2F, F^5)	93.6 (C^1), 109.5 (C^2), 108.5 (C^3), 118.4 (C^4)[c]	[5]
$C_6F_{13}IF_2$	CH_2Cl_2	−75.6 (2F, F^1), −81.2 (3F, F^6), −116.9 (2F, F^2), −121.6 (2F, F^3), −122.8 (2F, F^4), −126.4 (2F, F^5), −171.6 (2F, IF_2)		[5]
$C_6F_{13}IF_4$	PFB	−82.0 (2F, F^1), −81.4 (3F, F^6), −119.5 (2F, F^2), −121.2 (2F) and −122.4 (2F) (F^3 and F^4), −126.2 (2F, F^5), −27.7 (4F, IF_4)		[77]
$(CF_3)_2CFCF{=}CFIF_2$	CH_2Cl_2	*trans*: −75.5 (2CF_3), −122.8 (1F, F^1), −136.1 (1F, F^2), −188.4 (1F, F^3), −165.3 (2F, IF_2); *cis*: −75.1 (2CF_3), −102.0 (1F, F^1), −131.4 (1F, F^2), −180.8 (1F, F^3), −156.7 (2F, IF_2)		[5]
$(CF_3)_2CFCF{=}CFIF_4$	CH_2Cl_2	*trans*: −75.5 (2CF_3), −129.7 (1F, F^1), −145.0 (1F, F^2), −187.3 (1F, F^3), −19.7 (4F, IF_4); *cis*: −74.6 (2CF_3), −109.3 (1F, F^1), −134.9 (1F, F^2), −184.3 (1F, F^3), −12.3 (4F, IF_4)		[77]
C_6F_5I	$CDCl_3$	−120.1 (2F, F^{2,6}), −153.1 (1F, F^4), −160.3 (2F, F^{3,5})	66.1 (C^1), 147.0 (C^{2,6}), 136.9 (C^{3,5}), 141.4 (C^4)	[10]
$C_6F_5IF_2$	CD_2Cl_2	−122.1 (2F, F^{2,6}), −143.6 (1F, F^4), −156.9 (2F, F^{3,5}), −158.6 (2F, IF_2)	103.7 (C^1), 145.4 (C^{2,6}), 137.9 (C^{3,5}), 146.3 (C^4)	[10]
$C_6F_5IF_4$	CD_2Cl_2	−130.1 (2F, F^{2,6}), −143.3 (1F, F^4), −158.3 (2F, F^{3,5}), −9.0 (4F, IF_4)	132.3 (C^1), 145.6 (C^{2,6}), 138.7 (C^{3,5}), 145.4 (C^4)	[80]
$[(C_6F_{13})I(C_6H_5)]OTf$	$CDCl_3$	−70.5 (2F, F^1), −81.3 (3F, F^6), −114.2 (2F, F^2), −121.7 (2F, F^3), −123.0 (2F, F^4), −126.5 (2F, F^5)		[56]
$[(CF_2{=}CF)I(C_6F_5)][BF_4]$	CH_3CN	−77.2 (1F, F^2*trans*), −95.7 (1F, F^2*cis*), −157.0 (1F, F^1), −120.5 (2F, *F*^{2,6}), −140.9 (1F, *F*^{4}), −155.3 (2F, *F*^{3,5})[d]	103.2 (C^1), 156.3 (C^2), 85.8 (*C*^{1}), 147.3 (*C*^{2,6}), 138.5 (*C*^{3,5}), 147.4 (*C*^{4}),[d,e]	[21]
$[(C_6F_5)I(C_6H_5)][BF_4]$	CD_3CN	−121.1 (2F, F^{2,6}), −142.6 (1F, F^4), −155.9 (2F, F^{3,5})	87.1 (*C*^{1}), 147.5 (*C*^{2,6}), 138.8 (*C*^{3,5}), 146.8 (*C*^{4}),[d] 115.1 (C^1), 133.8 (C^{2,6}), 137.3 (C^{3,5}), 134.8 (C^4)	[65]
$[(C_6F_5)_2I][BF_4]$	CD_3CN	−120.4 (2F, F^{2,6}), −141.4 (1F, F^4), −155.7 (2F, F^{3,5})	88.4 (C^1), 147.7 (C^{2,6}), 138.9 (C^{3,5}), 147.5 (C^4)	[65]
$[(C_6F_5)_2IF_2][BF_4]$	CD_3CN	−125.4 (2F, F^{2,6}), −136.4 (1F, F^4), −153.7 (2F, F^{3,5}), −58.1 (2F, IF)	112.6 (C^1), 146.7 (C^{2,6}), 139.8 (C^{3,5}), 148.6 (C^4)	[26]

[a] Signals of counteranions were not presented. Numeration of F and C atoms starts from the Hal(III and V) position; F^1 is attached at C^1.

[b] In CD_3CN [104].

[c] ^{13}C NMR of C_4F_9I [128].

[d] *F* and *C* atoms marked in italics belong to the C_6F_5 group.

[e] In CD_3NO_2.

replaced by basic MeCN all signals of the pentafluorophenyl group of both $[(C_6F_5)_2Br][BF_4]$ and $[(C_6F_5)_2I][BF_4]$ were shifted to lower frequencies by 2–5 ppm. A similar shift tendency was observed in the spectra of the iodonium salts $[(CF_3C{\equiv}C)(C_6F_5)I][BF_4]$ (replacement of aHF by PFP) [18] or $[(C_6F_5)_2I][OTf]$ (replacement of CH_2Cl_2 by H_2O or MeCN) [58]. The influence of the counteranion on ^{19}F NMR shifts of iodonium salts was well demonstrated by Umemoto et al. in the series of $[(C_8F_{17})(C_6H_5)I]Y$ salts: the ^{19}F resonance of the α-difluoromethylene group moved from −68 to −74, −78, and −86 ppm when $Y = OS(O)_2CF_3$ was substituted by $OS(O)_2OH$, $OS(O)_2CH_3$, and Cl, respectively. It is in good agreement with the order of nucleofugality of Y^- and reflects the decreasing partial positive charge on iodine with increasing polarisability of the anion, Y^- [56].

The ^{13}C NMR resonances of the molecules, R_FHalF_m, and of the halonium salts, $[R'(R_F)Hal]Y$, show significantly deshielding of the carbon atoms relative to these in the parent compounds, R_FHal. Thus, the $\delta(C^1)$ shifts in CF_3CH_2I and $CF_3CH_2IF_2$ are −5.0 and 46.2 ppm, respectively [18]. The ^{13}C signals of CF_3IF_m are located at 79.5 ($m = 0$), 106.7 ($m = 2$), and 131.2 ($m = 4$) ppm (solutions in MeCN at 21, −20, and −30 °C, respectively) [129]. In the series of pentafluorophenyl derivatives the deshielding $\Delta\delta(C^1)$ is 23 and 55 ppm (Hal = Br), 38 and 66 ppm (Hal = I) for $m = 2$ and 4, respectively. The deshielding of C^4 is small (3–5 ppm), and $\Delta\delta(C^{2,6})$ and $\Delta\delta(C^{3,5})$ do not exceed 2 ppm (Table 1). Unfortunately, the ^{13}C NMR spectra of the majority of other perfluoroorganyliodine compounds, R_FIX_m ($R_F = C_nF_{2n+1}$, $R''CF = CF$, $R''C{\equiv}C$; $R'' \neq F$), were not reported.

In iodonium salts, $[R_F(R')I]Y$, ^{13}C resonances display less deshielding relative to the related R_FIF_m molecules. Thus, the deshielding $\Delta\delta(C^1)$ in $[(C_6F_5)_2Hal][BF_4]$ are only 6 (Hal = Br) and 22 (Hal = I) ppm (Table 1). Asymmetric pentafluorophenyliodonium salts, $[C_6F_5(R')I][BF_4]$, [65] show similar values of $\Delta\delta(C^1) = 20$–22 ppm, practically independent of the nature of the second ligand R′ (Table 1). The resonances of C^1 and C^2 of perfluoroalkynyliodonium salts $[(R_FC{\equiv}C)(R')I][BF_4]$ ($R_F = CF_3$, $(CF_3)_2CF$) are located at 20–30 ppm and 92–101 ppm, respectively (cf. $\delta(C^1) = 13.8$ and $\delta(C^2) = 81.4$ ppm in $CF_3C{\equiv}CI$) [18]. The influence of the substituent R_F on $\delta(C^1)$ and $\delta(C^2)$ in the alkynyliodonium cation of $[(F_3CC{\equiv}C)(CF_3CH_2)I][BF_4]$ ($\delta(C) = 20$ ($C{\equiv}C$–I) and 95 ($C{\equiv}C$–I) ppm [18]) is well demonstrated by a comparison with the non-fluorinated alkynyliodonium salt $[(CH_3)_3CC{\equiv}C)(CF_3CH_2)I][OTf]$ ($\delta(^{13}C) = -8.3$ ($C{\equiv}C$–I) and 102.9 ($C{\equiv}C$–I) ppm [61]).

6. Structural characteristics of polyvalent perfluoroorganoiodine(III and V) compounds

The molecular structure of polyvalent compounds of iodine and bromine(III and V) can be predicted by means of the VSEPR concept. Thus, $RHalX_2$ molecule have T-shape and $RHalX_4$ a square pyramidal shape, whereas their related cations $[R_2Hal]^+$ and $[R_2HalX_2]^+$ show a bent and a sawhorse geometry, respectively. For the two types of molecules and cations examples of crystal structures are known in case of iodine. In this chapter only trends observed for prototypes of perfluoroalkyl and perfluoroaryl derivatives are presented. Structural data for some polyfluoroalkyliodine(III) compounds are reported by Pennington and co-workers [131]. Besides molecular parameters we discuss also intermolecular interactions. With a CF_3 group attached to Hal(III and V) only structures of CF_3IX_n molecules, namely CF_3IF_2 [27], CF_3ICl_2 [102], $CF_3I(OMe)_2$ [99], $CF_3I(OC(O)CF_3)_2$ [132], $CF_3I(ONO_2)_2$ [133], $CF_3I(Cl)OMe$ [99], and CF_3IF_4 [76] are known up to now (Table 2). More different types are known with a C_6F_5 group bonded to Hal(III and V). Besides the molecules $C_6F_5IF_2$ [10], $C_6F_5IF_4$ [80], $C_6F_5I(OC(O)CF_3)_2$ [134], and $C_6F_5I(OC(O)C_6F_5)_2$ [135] (Table 2) salts with the cations $[(C_6F_5)_2I]^+$ [65] and $[(C_6F_5)_2IF_2]^+$ [26,113] were structurally characterised as well as bromonium salts with the related $[(C_6F_5)_2Br]^+$ cation [86] (Table 3). In case of CF_3IX_2 molecules, CF_3IF_2 shows the shortest average C–I distance and CF_3ICl_2 the longest. All $CF_3I(OY)_2$ molecules (Y = Me, $C(O)CF_3$, NO_2)

Table 2
Characteristic structural features of R_FIX_2 and R_FIX_4 molecules

R_FIX_n ($n = 2, 4$)	D(I–C) (Å)[a]	D(I–X) (Å)	D(I–X′) (Å)	$\angle$(C–I–X) (°)	$\angle$(C–I–X′) (°)	$\angle$(X–I–X) (°) or $\angle$(X–I–X′) (°)	Shortest intermolecular contact (I–X) or (I–X′) (Å)	Reference
CF_3IF_2	2.174(6)	1.982(2)	–	82.71(9)	–	165.4(2)	2.950	[27]
CF_3ICl_2	2.229(10)	2.457(2)–2.478(2)	–	82.9(3)–88.7(3)	–	171.62(9)	3.324(3)	[102]
$CF_3I(OMe)_2$	2.190(12)	2.019(11)–2.087(11)	–	81.4(5)	–	166.7(4)	2.749(9)	[99]
$CF_3I(Cl)OMe$	2.207(7)–2.212(8)	1.969(5)–1.991(5)[b]	2.578(2)–2.580(2)[c]	89.2(2)–89.3(3)	81.7(2)–82.0(2)	171.0(2)	3.104(2)[c], 3.235(5)[b]	[99]
$CF_3I(O_2CCF_3)_2$	2.209(3)	2.094(2)–2.160(2)		77.42(10)–86.52(10)		163.51(8)	2.913(2)	[126]
$CF_3I(ONO_2)_2$	2.212(4)	2.073(3)–2.208(2)	–	76.3(1)–89.2(1)	–	165.3(1)	3.160(3)	[127]
CF_3IF_4	2.22(1)	1.904(6)–1.925(5)	–	80.9(3)–83.6(4)	–	87.5(2)–89.5(3)	3.079(6)	[76]
$C_6F_5IF_2$	2.068(3)–2.068(3)	1.950(3)–2.032(2)	–	83.29(12)–87.39(13)	–	170.46(10)–171.59(9)	2.742(2)	[10]
$C_6F_5I(CN)F$	2.077(3)[d]	2.110(2)[e]	2.112(4)[f]	80.95(11)	86.27(14)	167.09(12)	2.644(2)[g]	[100]
$C_6F_5I(O_2CCF_3)_2$	2.063(6)–2.078(10)	2.128(6)–2.147(6)		80.8(3)–82.2(3)		162.6(3)–163.0(2)	2.918(9)	[128]
$C_6F_5I(O_2CC_6F_5)_2$	2.072(4)	2.107(2)–2.140(2)	–	83.27(12)–84.93(12)	–	168.19(12)	3.127(3)[h]	[129]
$C_6F_5IF_4$	2.081(7)–2.088(5)	1.904(3)–1.929(4)	–	83.1(2)–84.7(1)	–	88.5(2)–90.4(2)	3.220(4)	[80]
$C_6F_5IOF_2$	2.095(8)–2.111(8)	1.901(8)–1.990(7)[i]	1.762(6)–1.770(7)[j]			167.4(2)[k] 89.0(3)–92.1(3)[l]	2,855	[107]

[a] For comparison: C–I in C_6F_5I [80] 2.077(4) Å.
[b] I–O.
[c] I–Cl.
[d] I–C_6F_5.
[e] I–F.
[f] I–CN.
[g] I–F.
[h] I–O (intramolecular).
[i] I–F.
[j] I = O.
[k] $\angle$(F–I–F).
[l] $\angle$(F–I = O).

Table 3

Characteristic structural features of the iodonium cations $[(C_6F_5)_2I]^+$ and $[(C_6F_5)_2IF_2]^+$ and of the formaly related molecule $C_6F_5I(CN)F$ and of the bromonium cation $[(C_6F_5)_2Br]^+$

$[(C_6F_5)_2IF_n]^+$ ($n = 0, 2$)	D(Hal-C) (Å)	D(Hal-F) (Å)	∠(C-Hal-C) (°)	∠(C-Hal-F) (°)	∠(F-Hal-F) (°)	Shortest contact cation-anion (Å)	Reference
$[(C_6F_5)_2I][BF_4]$	2.04(1)[a]–2.08(1)	–	94.9(5)	–	–	2.766(16)[b]	[65]
$[(C_6F_5)_2IF_2][BF_4]\cdot CH_2Cl_2$	2.047(5)–2.081(4)[a]	1.902(3)–1.923(3)	102.71(19)	84.37(16)–86.83(16)	166.54(13)	2.601(4)	[26]
$C_6F_5I(CN)F$	2.077(3)[a,c]–2.112(4)[d]	2.110(2)	86.27(14)	80.95(11)	–	2.644(2)[e]	[100]
$[(C_6F_5)_2Br][BF_4]$	1.894(8)–1.908(8)[f]	–	97.8(3)	–	–	2.791(8)	[86]

[a] Hal = I.
[b] I–FBF_3.
[c] I–C_6F_5.
[d] I–CN.
[e] I–F.
[f] Hal = Br.

have slightly longer C-I distances than CF_3IF_2. The C–I–X angles cover a range from 76.3 to 89.2° and their averaged values from 81.4 to 85.8°. The latter is associated with greater chlorine, whereas in case of fluorine and oxygen ligands the angle is close to 82°. When going from CF_3IF_2 to CF_3IF_4 the C–I–F angle does not change within 3σ, but the C–I distance becomes longer. This elongation may be attributed to the weakening of the C–I bond caused by the increase of partial positive charge on I(V) in combination with the partial positive charge on carbon.

In case of C_6F_5I(III and V) compounds the influence of the oxidation state of iodine, of the nature of the compound (neutral molecule or cation in a salt) on the structural parameters can be shown. Thus, the averaged C–I distance increases from $C_6F_5IF_2$ (2.068(3) Å) via C_6F_5I (2.077(4) Å) to $C_6F_5IF_4$ (2.085(7) Å) and is independent from the oxidation state of iodine for $[(C_6F_5)_2I]^+$ (2.06(1) Å) and $[(C_6F_5)_2IF_2]^+$ (2.064(5) Å) (both as $[BF_4]^-$ salts) (Table 3). The averaged I-F distance becomes shorter from $C_6F_5IF_2$ (1.991(3) Å) to $C_6F_5IF_4$ (1.917(4) Å) and neglectable shorter when going to the I(V) cation $[(C_6F_5)_2IF_2]^+$ (1.913 (3) Å). In $[(C_6F_5)_2IF_2]^+$ the C–I–C angle is greater by 7.8° in comparison with $[(C_6F_5)_2I]^+$. The F–I–F angle in $[(C_6F_5)_2IF_2][BF_4]$ is 4.5° smaller than that in neutral $C_6F_5IF_2$.

A characteristic feature of all above mentioned perfluoroorganoiodine(III and V) compounds are intermolecular contacts which are caused by the significant partial positive charge on iodine. These contacts with nucleophilic sites are strong in R_FIF_n molecules ($n = 2, 4$) and in iodonium salts. So far the shortest I- -F contact of 2.601(4) Å was observed in $[(C_6F_5)_2IF_2][BF_4]\cdot CH_2Cl_2$ (sum of van der Waals radii I–F = 3.45 Å [136]). Some authors e.g. Ochiai [137] describe iodonium(III) salts, [RR′I]Y, as λ^3-iodanes even with I- -Y contacts of approximately 3.0 ± 0.2 Å and explain their view by the T-shape environment of iodine. From their physical and chemical properties iodonium salts are no molecules. Their electrophilic cations have an octet and their contacts to anions correlate with the electrophilicity of the cation and the nucleophilicity of the anion. Thus, in perfluoroorganoiodonium salts these electrostatic contacts are most distinct. An interesting compound relating to the present topic is $C_6F_5I(CN)F$ [100], which can be described by three Lewis formula: $[C_6F_5(CN)I]F$ (a), $[C_6F_5(F)I][CN]$ (b), and $C_6F_5I(CN)F$ (c). Formula a and b express the iodonium character and c the T-shape molecule, where CN acts as a pseudo-halogen. Here the structural parameters support formula c (Table 2).

7. Summary

This review has shown relations between perfluoroorganoiodine and -bromine compounds and their parent molecules $HalF_x$ ($x = 3$ and 5). R_FHalF_2 and R_FHalF_4 are intensively investigated derivatives which are preferentially used for transformations in the Hal-F moiety. Neutral R_FHalF_2 and R_FHalF_4 molecules (Hal = I, Br) can principally be obtained on nucleophilic routes from the halogen fluorides and suitable R_F-transfer reagents. The majority of R_FIF_2 and R_FIF_4 were prepared by oxidative addition of fluorine. The oxidative addition can be extended to ROOR and restricted to Cl_2. ClX reagents (X = F, OR_F, ONO_2, $OS(O_2)F$, OCl, $OClO_3$, and $OTeF_5$) allow the synthesis of a wide variety of R_FIX_2 compounds. R_FIF_2 and $R_FI(OC(O)R'_F)_2$ are suitable starting materials to introduce preferentially carbon and oxygen nucleophiles into the iodine(III) moiety. Applications mainly use the fluorination property of R_FIF_2 or the oxidation property of R_FIX_2. Iodonium and bromonium(III) salts $[R_F(R)Hal]Y$ were prepared under acidic conditions. Their electrophilic cations allow the formal transfer of R_F cations to nucleophiles. In case of $[(R_F)_2IF_2]Y$ the excellent fluorination potential is worth to mention.

Besides the reported material the review reveals "white spots" of fundamental research like the preparation of perfluoroorganoiodine(VII) or -chlorine(III and V) compounds. Furthermore, it shows that in contrast to polyvalent non-fluorinated iodine compounds the perfluorinated analogues are less wide-spread investigated (a) as reagents in fluoroorganic chemistry and (b) with application purposes.

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References

[1] (a) A.E. Reed, P.v.R. Schleyer, J. Am. Chem. Soc. 112 (1990) 1434–1445;
(b) W. Kutzelnigg, Angew. Chem. Intern. Ed. Engl. 23 (1984) 272–295;
(c) J.L. Musher, Angew. Chem. 81 (1969) 68–83.

[2] Selected reviews:
(a) E.D. Matveeva, M.V. Proskurnina, N.S. Zefirov, Heteroatom Chem. 17 (2006) 595–617;
(b) P.J. Stang, J. Org. Chem. 68 (2003) 2997–3008;
(c) V.V. Zhdankin, P.J. Stang, Chem. Rev. 102 (2002) 2523–2584;
(d) N.S. Pirkuliev, V.K. Brel, N.S. Zefirov, Usp. Khim. 69 (2000) 118–133, Russ. Chem. Rev. 69 (2000) 105–120;
(e) T. Umemoto, Chem. Rev. 96 (1996) 1757–1778;
(f) P.J. Stang, V.V. Zhdankin, Chem. Rev. 96 (1996) 1123–1178;
(g) I.I. Maletina, V.V. Orda, L.M. Yagupol'skii, Usp. Khim. 58 (1989) 925–950, Russ. Chem. Rev. 58 (1989) 544–558;
(h) E.B. Merkushev, Usp. Khim. 56 (1987) 1444–1479, Russ. Chem. Rev. 56 (1987) 826–845;
(i) I.I. Maletina, A.A. Mironova, V.V. Orda, L.M. Yagupol'skii, Rev. Heteroatom Chem. 8 (1993) 232–255;
(j) V.V. Zhdankin, Hypervalent Iodoarenes and Arene Iodonium Salts in Science of Synthesis, Houben-Weyl Methods of Molecular Transformations, vol. 31a, 2007, Chapter 31.4.1;

(k) T. Wirth, Topics in Current Chemistry: Hypervalent Iodine Chemistry, vol. 224, Springer, Berlin, 2003, p. 1;
(l) K.-Y. Akiba, Chemistry of Hypervalent Compounds, Wiley-VCH, New York, 1999;
(m) A. Varvoglis, Hypervalent Iodine in Organic Synthesis, Academic Press, London, 1997;
(n) A. Varvoglis, The Organic Chemistry of Polycoordinated Iodine, VCH, Weinheim, 1992.
[3] M. Schmeißer, E. Scharf, Angew. Chem. 71 (1959) 524.
[4] D. Naumann, M. Schmeißer, L. Deneken, J. Inorg. Nucl. Chem. Suppl. (1976) 13–15.
[5] F. Bailly, Perfluororganoiod(III)-Verbindungen, Dissertation, University Duisburg, 2001, ISBN 3-89833-039-7.
[6] C.S. Rondesvedt, J. Am. Chem. Soc. 91 (1969) 3054–3061.
[7] D. Naumann, L. Deneken, J. Fluorine Chem. 5 (1975) 443–447.
[8] H.-J. Frohn, R. Nielinger, J. Fluorine Chem. 77 (1996) 143–146.
[9] M. Schmeißer, K. Dahmen, P. Sartori, Chem. Ber. 103 (1970) 307–311.
[10] F. Bailly, P. Barthen, W. Breuer, H.-J. Frohn, M. Giesen, J. Helber, G. Henkel, A. Priwitzer, Z. Anorg. Allg. Chem. 626 (2000) 1406–1413.
[11] V. Padelidakis, W. Tyrra, D. Naumann, J. Fluorine Chem. 99 (1999) 9–15.
[12] V.V. Lyalin, V.V. Orda, L.A. Alekseeva, L.M. Yagupol'skii, Zh. Org. Khim. 6 (1970) 329–332, J. Org. Chem. USSR 6 (1970) 317–319.
[13] D. Naumann, private communication.
[14] H.-J. Frohn, J. Helber, J. Fluorine Chem. 16 (1980) 568.
[15] P. Bravo, V. Montanari, G. Resnati, D.D. DesMarteau, J. Org. Chem. 59 (1994) 6093–6094.
[16] A.V. Fokin, Yu.N. Studnev, A.I. Rapkin, T.M. Potarina, L.D. Kuznetsova, Izv. Akad. Nauk SSSR, Ser. Khim. 11 (1980) 2641–2643.
[17] I.I. Maletina, V.V. Orda, N.N. Aleinikov, B.L. Korsunskii, L.M. Yagupol'skii, Zh. Org. Khim. 12 (1976) 1371–1372, J. Org. Chem. USSR 12 (1976) 1364.
[18] H.-J. Frohn, V.V. Bardin, Z. Anorg. Allg. Chem. 634 (2008) 82–86.
[19] K. Alam, A.F. Janzen, J. Fluorine Chem. 36 (1987) 179–184.
[20] H.-J. Frohn, V.V. Bardin, Z. Naturforsch. 51b (1996) 1015–1021.
[21] A. Abo-Amer, H.-J. Frohn, C. Steinberg, U. Westphal, J. Fluorine Chem. 127 (2006) 1311–1323.
[22] H.-J. Frohn, N. LeBlond, K. Lutar, B. Zemva, Angew. Chem. Int. Ed. Engl. 39 (2000) 391–393.
[23] C.S. Rondesvedt, US 3,377,390 (1968).
[24] C.S. Rondestvedt, FR 1521775 (1968).
[25] A. Wenda, H.-J. Frohn, U. Flörke, 15th European Symposium on Fluorine Chemistry, Prague (Czech Republic), 2007, p. 342, Abstract.
[26] H.-J. Frohn, A. Wenda, Z. Anorg. Allg. Chem. 634 (2008) 764–770.
[27] R. Minkwitz, M. Berkei, Inorg. Chem. 37 (1998) 5247–5250.
[28] R. Minkwitz, R. Bröchler, M. Schütze, Z. Anorg. Allg. Chem. 621 (1995) 1727–1730.
[29] J.A.M. Canich, M.E. Lerchen, G.L. Gard, J.M. Shreeve, Inorg. Chem. 25 (1986) 3030–3033.
[30] D. Naumann, H.H. Heinsen, E. Lehmann, J. Fluorine Chem. 8 (1976) 243–253.
[31] M. Schmeißer, E. Lehmann, D. Naumann, Chem. Ber. 110 (1977) 2665–2668.
[32] C.J. Schack, K.O. Christe, J. Fluorine Chem. 16 (1980) 63–73.
[33] C.J. Schack, D. Pilipovich, K.O. Christe, Inorg. Chem. 14 (1975) 145–151.
[34] C.J. Schack, K.O. Christe, J. Fluorine Chem. 47 (1990) 79–87.
[35] D. Naumann, L. Deneken, E. Renk, J. Fluorine Chem. 5 (1975) 509–519.
[36] M. Schmeißer, K. Dahmen, P. Sartori, Chem. Ber. 100 (1967) 1633–1637.
[37] V.V. Lyalin, V.V. Orda, L.A. Alekseeva, L.M. Yagupol'skii, Zh. Org. Khim. 8 (1972) 1019–1023, J. Org. Chem. USSR 8 (1972) 1027–1031.
[38] A.A. Mironova, I.I. Maletina, V.V. Orda, L.M. Yagupol'skii, Zh. Org. Khim. 19 (1983) 1213–1217, J. Org. Chem. USSR (1983) 1082–1085.
[39] J.P. Collman, Chem. Eng. News 63 (1985) 2.
[40] J. Helber, H.-J. Frohn, A. Klose, T. Scholten, Arkivoc Online Vers.: http://www.arkat-usa.org/ark/journal/2003/Varvoglis/AV-682A/682.htm.
[41] K. Dahmen, Dissertation, RWTH Aachen, 1967.
[42] (a) M. Schmeißer, E. Scharf, Angew. Chem. 72 (1960) 324;
(b) M. Schmeißer, P. Sartori, D. Naumann, Chem. Ber. 103 (1970) 590–593.
[43] H.-J. Frohn, K. Schrinner, Z. Anorg. Allg. Chem. 623 (1997) 1847–1849.
[44] W. Tyrra, D. Naumann, Can. J. Chem. 69 (1991) 327–333.
[45] D. Naumann, R. Feist, J. Fluorine Chem. 15 (1980) 541–542.
[46] H.-J. Frohn, P. Barthen, F. Bailly, K. Koppe, in: Proceedings of the First International Conference on Hypervalent Iodine, Thessaloniki, GR, (2001), pp. 109–111.
[47] L.M. Yagupol'skii, A.A. Mironova, I.I. Maletina, V.V. Orda, Zh. Org. Khim. 16 (1980) 232–233.
[48] I.I. Maletina, V.V. Orda, Y.L. Yagupol'skii, J. Fluorine Chem. 70 (1995) 85–88.
[49] V.V. Bardin, G.G. Furin, G.G. Yakobson, Zh. Obshch. Khim. 16 (1980) 1498–1501, J. Gen. Chem. USSR 16 (1980) 1288–1291.
[50] R. Minkwitz, V. Gerhard, Z. Naturforsch. 46b (1991) 884–886.
[51] G.A. Olah, Y.K. Mo, E.G. Melby, H.C. Lin, J. Org. Chem. 38 (1973) 367–372.
[52] H.-J. Frohn, V.V. Bardin, in: Proceedings of the 18th International Symposium on Fluorine Chemistry, Bremen (Germany), (2006), p. 92, Abstract.
[53] D. Naumann, W. Tyrra, J. Chem. Soc. Chem. Commun. (1989) 47–50.
[54] H. Butler, D. Naumann, W. Tyrra, Eur. J. Solid State Inorg. Chem. 29 (1992) 739–758.
[55] V.V. Lyalin, V.V. Orda, L.A. Alekseeva, L.M. Yagupol'skii, Zh. Org. Khim. 7 (1971) 1473–1478, J. Org. Chem. USSR 7 (1971) 1524–1527.
[56] T. Umemoto, Y. Kuriu, H. Shuyama, O. Miyano, S.-I. Nakayama, J. Fluorine Chem. 31 (1986) 37–56.
[57] T. Umemoto, Y. Gotoh, J. Fluorine Chem. 28 (1985) 235–239.
[58] W. Tyrra, H. Butler, D. Naumann, J. Fluorine Chem. 60 (1993) 79–83.
[59] V.V. Zhdankin, C.J. Kuehl, J.T. Bolz, N.S. Zefirov, Mendeleev Commun. (1994) 165–166.
[60] C.J. Kuehl, J.T. Bolz, V.V. Zhdankin, Synthesis (1995) 312–316.
[61] V.V. Zhdankin, C.J. Kuehl, A.J. Simonsen, J. Org. Chem. 61 (1996) 8272–8276.
[62] H.-J. Frohn, A. Klose, V.V. Bardin, J. Fluorine Chem. 64 (1993) 201–215.
[63] V.V. Bardin, H.-J. Frohn, Main Group Metal Chem. 25 (2002) 589–613.
[64] V.V. Bardin, N.Yu. Adonin, H.-J. Frohn, J. Fluorine Chem. 128 (2007) 699–702.
[65] F. Bailly, P. Barthen, H.-J. Frohn, M. Köckerling, Z. Anorg. Allg. Chem. 626 (2000) 2419–2427.
[66] A. Abo-Amer, N.Y. Adonin, V.V. Bardin, P. Fritzen, H.-J. Frohn, C. Steinberg, J. Fluorine Chem. 125 (2004) 1771–1778.
[67] H.-J. Frohn, V.V. Bardin, M. Becher, V. Bilir, U. Flörke, 15th European Symposium on Fluorine Chemistry, Prague (Czech Republic), 2007, p. 95, Abstract.
[68] T. Lewe, W. Tyrra, D. Naumann, J. Fluorine Chem. 99 (1999) 123–125.
[69] H.-J. Frohn, M. Giesen, A. Klose, A. Lewin, V.V. Bardin, J. Organomet. Chem. 506 (1996) 155–164.
[70] W. Tyrra, D. Naumann, J. Fluorine Chem. 45 (1989) 401–416.
[71] G. Oates, J.M. Winfield, J. Chem. Soc. Dalton Trans. (1974) 119–124.
[72] O.R. Chambers, G. Oates, J.M. Winfield, J. Chem. Soc. Commun. (1972) 839–840.
[73] G. Oates, J.M. Winfield, J. Fluorine Chem. 4 (1974) 235–237.
[74] J.A. Berry, G. Oates, J.M. Winfield, J. Chem. Soc. Dalton Trans. (1974) 509–511.
[75] C. Steinberg, Dissertation, University Duisburg-Essen, 2008.
[76] R. Minkwitz, R. Bröchler, H. Preut, Z. Anorg. Allg. Chem. 621 (1995) 1247–1250.
[77] H.-J. Frohn, V.V. Bardin, J. Fluorine Chem. 126 (2005) 1036–1043.
[78] H.-J. Frohn, Chem.-Ztg. 108 (1984) 146–147.
[79] H.-J. Frohn, V.V. Bardin, J. Organomet. Chem. 501 (1995) 155–159.
[80] H.-J. Frohn, S. Görg, G. Henkel, M. Läge, Z. Anorg. Allg. Chem. 621 (1995) 1251–1256.
[81] T. Lewe, D. Naumann, G. Nowicki, H. Schneider, W. Tyrra, Z. Anorg. Allg. Chem. 623 (1997) 122–128.
[82] W. Tyrra, D. Naumann, Can. J. Chem. 67 (1989) 1949–1951.
[83] V.V. Bardin, G.G. Furin, G.G. Yakobson, Zh. Org. Khim. 16 (1980) 1256–1263, J. Org. Chem. USSR 16 (1980) 1086–1092.
[84] J.A. Obaleye, L.C. Sams, J. Inorg. Nucl. Chem. 43 (1981) 2259–2260.
[85] H.-J. Frohn, M. Giesen, J. Fluorine Chem. 24 (1984) 9–15.
[86] H.-J. Frohn, M. Giesen, D. Welting, Eur. J. Solid State Inorg. Chem. 33 (1996) 841–853.
[87] A.N. Nesmeyanov, A.N. Vanchikov, I.N. Lisichkina, V.V. Grushin, T.P. Tolstaya, Dokl. Akad. Nauk SSSR 255 (1980) 1386–1389, Proc. Acad. Sci. USSR (1980) 606–609.
[88] A.N. Nesmeyanov, A.N. Vanchikov, I.N. Lisichkina, V.V. Lazarev, T.P. Tolstaya, Dokl. Akad. Nauk SSSR 255 (1980) 1136–1140, Proc. Acad. Sci. USSR (1980) 594–598.
[89] V.V. Bardin, H.-J. Frohn, in: Proceedings of the 18th International Symposium on Fluorine Chemistry, Bremen (Germany), (2006), p. 301, Abstract.
[90] J.A. Obaleye, L.C. Sams, J. Inorg. Nucl. Chem. Lett. 16 (1980) 343–347.
[91] M.H. Habibi, L.C. Sams, J. Fluorine Chem. 18 (1981) 277–280.
[92] M.H. Habibi, L.C. Sams, J. Fluorine Chem. 21 (1982) 287–293.
[93] H.-J. Frohn, W. Breuer, J. Fluorine Chem. 34 (1987) 443–451.
[94] W. Breuer, H.-J. Frohn, J. Fluorine Chem. 47 (1990) 301–315.
[95] W. Breuer, H.-J. Frohn, Z. Anorg. Allg. Chem. 619 (1993) 209–214.
[96] W. Breuer, H.-J. Frohn, Z. Anorg. Allg. Chem. 611 (1992) 85–91.
[97] J.A. Obaleye, L.C. Sams, J. Fluorine Chem. 18 (1981) 31–35.
[98] J.A. Obaleye, L.C. Sams, J. Fluorine Chem. 24 (1984) 413–418.
[99] R. Minkwitz, M. Berkei, R. Ludwig, Eur. J. Inorg. Chem. (2000) 2387–2392.
[100] (a) H.-J. Frohn, M. Hirschberg, in: Proceedings of the Second International Conference on Hypervalent Iodine, Thessaloniki, GR, (2006), pp. 1–3;
(b) M. Hirschberg, H.-J. Frohn, in: Proceedings of the 18th International Symposium on Fluorine Chemistry, Bremen (Germany), (2006), p. 238, Abstract.
[101] H.-J. Frohn, U. Flörke, M. Hirschberg, in: Proceedings of the 15th European Symposium on Fluorine Chemistry, Prague (Czech Republic), 2007, p. 310, Abstract.
[102] R. Minkwitz, M. Berkei, Inorg. Chem. 38 (1999) 5041–5044.
[103] D. Naumann, J. Baumanns, J. Fluorine Chem. 8 (1976) 177–182.
[104] M. Giesen, Dissertation, University Duisburg, 1986.
[105] V.V. Zhdankin, C.J. Kuehl, A.J. Simonsen, Main Group Chem. 1 (1996) 349–352.
[106] V.V. Zhdankin, C.J. Kuehl, Tetrahedron Lett. 35 (1994) 1809–1812.
[107] S. Görg, Dissertation, University Duisburg, 1994.
[108] Z.-Q. Tian, J.L. Richards, T.G. Traylor, J. Am. Chem. Soc. 117 (1995) 21–29.
[109] H. Volz, W. Müller, Liebigs Ann. Chem. (1992) 1097–1101.
[110] D. Naumann, W. Habel, Z. Anorg. Allg. Chem. 482 (1981) 139–142.
[111] V.V. Lyalin, V.V. Orda, L.A. Alekseeva, L.M. Yagupol'skii, SU 283203 19701006, USSR (1970).
[112] J. Baumanns, L. Deneken, D. Naumann, M. Schmeißer, J. Fluorine Chem. 3 (1973/1974) 323–327.
[113] A. Wenda, H.-J. Frohn, in: Proceedings of the 18th International Symposium on Fluorine Chemistry, Bremen (Germany), (2006), p. 237, Abstract.
[114] H.-J. Frohn, V.V. Bardin, J. Fluorine Chem. 127 (2006) 18–21.
[115] A.A. Mironova, I.I. Maletina, V.V. Orda, L.M. Yagupol'skii, Zh. Org. Khim. 26 (1990) 549–553.
[116] A.A. Mironova, V.V. Orda, I.I. Maletina, L.M. Yagupol'skii, Zh. Org. Khim. 25 (1989) 665–666, J. Org. Chem. USSR 25 (1989) 597–598.
[117] J. Zhang, G.R. Martin, D.D. DesMarteau, Chem. Commun. (2003) 2334–2335.

[118] S.A. Klyuchinskii, S.B. Grishnyakov, L.V. Demchenko, V.S. Zavgorodnii, Zh. Obshch. Khim. 63 (1993) 2394–2395, Russ. J. Gen. Chem. 63 (1993) 1661–1662.
[119] T. Umemoto, Y. Gotoh, Bull. Chem. Soc. Jpn. 59 (1986) 439–445.
[120] D.D. DesMarteau, V. Montanari, Chem. Commun. (1998) 2241–2242.
[121] P. Eisenberger, S. Gischig, A. Togni, Chem. Eur. J. 12 (2006) 2579–2586.
[122] I. Kieltsch, P. Eisenberger, A. Togni, Angew. Chem. Int. Ed. 46 (2007) 754–757.
[123] S.A. Lermontov, T.N. Velikohat'ko, N.S. Zefirov, Izv. Akad. Nauk Ser. Khim. 45 (1996) 1022–1023, Russ. Chem. Bull. 45 (1996) 977–978.
[124] V. Tesevic, J.A. Gladysz, Green Chem. 7 (2005) 833–836.
[125] V. Montanari, K. Kumar, J. Am. Chem. Soc. 126 (2004) 9528–9529.
[126] V. Montanari, K. Kumar, J. Fluorine Chem. 127 (2006) 565–570.
[127] V. Montanari, K. Kumar, Eur. J. Org. Chem. (2006) 874–877.
[128] H.-O. Kalinowski, S. Berger, S. Braun, ^{13}C-NMR-Spektroskopie. Thieme, 1984, Stuttgart/NY.
[129] W. Tyrra, M. Miczka, D. Naumann, Z. Anorg. Allg. Chem. 623 (1997) 1857–1859.
[130] As a convention, shielding (deshielding) of atoms in the NMR spectra of polyvalent halogen compound is related to the corresponding monovalent halogen compound. For instance, $\Delta\delta(C^1) = \delta(C^1)(CF_3IF_m) - \delta(C^1)(CF_3I)$.
[131] V. Montanari, D.D. DesMarteau, W.T. Pennington, J. Mol. Struct. 550/551 (2000) 337–348.
[132] R. Minkwitz, M. Berkei, Z. Naturforsch. 55b (2000) 718–722.
[133] R. Minkwitz, T. Hertel, H. Preut, Z. Anorg. Allg. Chem. 621 (1995) 1552–1557.
[134] M. Bardan, T. Birchall, C.S. Frampton, P. Kapoor, Can. J. Chem. 67 (1989) 1878–1885.
[135] H.-J. Frohn, J. Helber, A. Richter, Chem. Ztg. 107 (1983) 169–172.
[136] A. Bondi, J. Phys. Chem. 68 (1964) 441–451.
[137] M. Ochiai, in: K.-Y. Akiba (Ed.), Organic Synthesis Using Hypervalent Organoiodanes in Chemistry of Hypervalent Compounds, Wiley-VCH, New York, 1999, pp. 359–387.