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Review

Advances in the preparation of organofluorine compounds involving iodine and/or iodo-compounds

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Abstract

The intriguing properties of iodine have drawn the attention of organic chemists. In this paper, we will describe the recent development of stereo- and/or regioselective synthesis of fluorine-containing organic compounds employing hypervalent iodine fluorides such as $ArIF_2$ (**1**), IF_5 (**22**), and (*E*)-2-fluoro-alk-1-enyl-4-aryl iodonium salts R(F)C=C(H)IF–Ar (**12**). The electrochemical fluorination procedures involving iodo-compounds will also be presented to prepare fluoro-organic compounds.
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Keywords: Fluorination; Iodofluorination; Deiodinative fluorination; Hypervalent iodine fluorides; Iodoarene difluoride ($ArIF_2$); Iodine pentafluoride (IF_5); (*E*)-2-Fluoro-alk-1-enyl-4-aryl iodonium salts; Electrochemical fluorination; (*E*)-α-Fluoro-β-substituted alkene

1. Infroduction

Iodine is a rare element known for centuries. In recent years, the intriguing properties of iodine have drawn the attention of organic chemists [1]. In the field of organofluorine chemistry, the iodofluorination of cyclohexene and various unsaturated steroids was first carried out [2,3] using *N*-iodosuccinimide (NIS) and HF in the presence of ether [4], and later on, some chemists found interesting fluorination modes using *N*-iodoimides with HF-combined base solutions [5–15] such as HF-pyridine [6]. The iodofluorination of unsaturated bonds is well established to occur through in situ generated iodine fluoride (''IF'') from a solution consisting of *N*-iodoimides as an iodonium ion (I^+) source and hexafluoropropene–Et_2NH [16] as well as HF-combined base solutions as a fluoride ion (F^-) source. The iodofluorination of unsaturated bonds has also been successfully carried out using other systems such as I_2 with AgF [17–20], I_2 with diluted F_2 in N_2, [21–24], I_2 with IF_5 [25], $I(Py)_2BF_4$ [26,27], and $I^+(collidine)_2BF_4^-$ [28]. On the other hand, by employing a system using reagents for the iodofluorination of unsaturated bonds such as NIS and HF-combined base solutions, 1,3-dithiolanes [29–31] and hydrazones [32–35] can be transformed to their corresponding *gem*-difluoride. Also, the oxidative desulfurization–fluorination [36–38] of thiocarboxylic *O*-acid esters, *O*,*O*′-disubstituted thiocarbonate [35], and arenedithiocarboxylic [36] has been successfully performed to produce the corresponding *gem*-difluoro-compounds, trifluoromethyl-substituted aromatic compounds, and α-fluorosulfides, respectively.

In this study, the recent progress in the methodology will be discussed for the preparation of fluoro-organic compounds making use of iodine and/or its compounds.

2. Fluorination of organic compounds with hypervalent iodine fluorides

2.1. Iodoarene difluoride ($ArIF_2$) and its use as fluorination reagent

2.1.1. Preparation of $ArIF_2$

Iodoarene difluoride ($ArIF_2$) (**1**) is chemically prepared by the Carpenter [39] or Zupan and Pollak [40] method (Eqs. (1) and (2)). On the other hand, we have recently developed a more convenient procedure without using hazardous chemicals such as HgO and/or XeF_2 (Eq. (3)) [41].

$$ArI \xrightarrow{Cl_2} ArICl_2 \xrightarrow[HF_{aq}]{HgO} \underset{\mathbf{1}}{ArIF_2} \quad (1)$$

$$ArI \xrightarrow{XeF_2} \underset{\mathbf{1}}{ArIF_2} \quad (2)$$

$$ArICl_2 \xrightarrow[THF]{NaOHaq} ArI{=}O \xrightarrow[CH_2Cl_2]{HFaq} \underset{\mathbf{1}\ \text{Y: ~ 80\%}}{ArIF_2} \quad (3)$$

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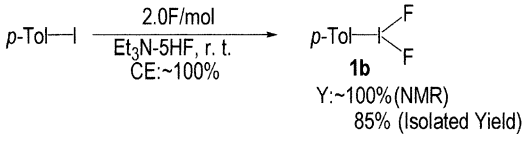
The anodic oxidation of ArI in an HF-base electrolyte may also yield **1** such as *p*-$NO_2C_6H_4IF_2$ and *p*-$MeOC_6H_4IF_2$ [42] using Et_3N–3HF [43] as an electrolyte. However, these products were too unstable to isolate and the attempt for the preparation of *p*-$CH_3C_6H_4IF_2$ (**1b**) from *p*-iodotoluene under similar conditions was a failure. In contrast, the anodic oxidation of *p*-iodotoluene was successfully performed quantitatively affording **1b** with a high current efficiency [44] in Et_3N–5HF[1] as the electrolyte by employing a divided cell made of Teflon PFA[2] equipped with Nafion 117 film as a diaphragm using two smooth Pt sheets (20 mm × 20 mm) for the anode and cathode under a nitrogen atmosphere. Incidentally, the compound **1b** thus produced was readily extracted using CH_2Cl_2 and was isolated as a white powder in yields of more than 85% (Eq. (4)).

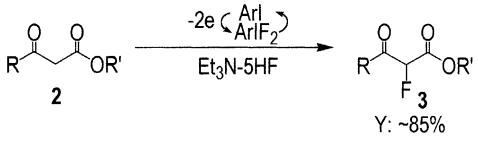


(4)

2.1.2. Fluorination of β-ketoesters

The solution of **1** in Et_3N–5HF thus obtained electrochemically can be used in situ as a useful fluorination reagent for various organic compounds. β-Ketoesters (**2**) reacted with **1** such as *p*-$NO_2C_6H_4IF_2$, *p*-$MeOC_6H_4IF_2$, $PhIF_2$, and **1b** to produce α-fluoro-β-ketoesters (**3**) selectively in the presence of Et_3N–5HF [53]. Satisfactory results are obtained in the reaction of **2** with **1b** to produce **3** in high yields under the mild conditions shown in Scheme 1. Compound **1b** alone, however, showed no reactivity towards **2**.[3]

We expect to successfully carry out the indirect electrochemical fluorination of **2** with ArI as an in-cell mediator producing the corresponding fluorinated compounds **3** (Eq. (5)). By carrying out the reaction in the anode compartment of an H-type divided cell under the conditions of constant-potential (1.5 V versus Ag/Ag^+) electrolysis, **3** was obtained in quite high yields (<85%) with a high current efficiency (<80%) [44]. Et_3N–5HF was again found to be an excellent electrolyte in this indirect electrochemical fluorination of **2**.

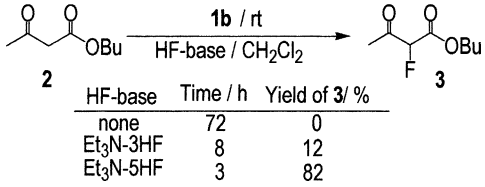


(5)

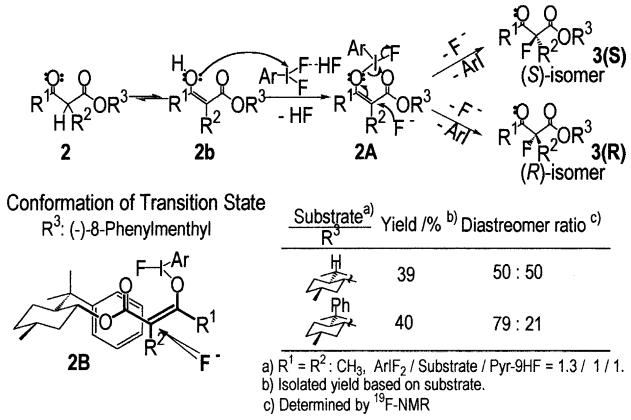
[1] Et_3N–5HF was prepared by the addition of freshly distilled Et_3N to 5 eqiv. of anhydrous HF in a Teflon PFA (footnote 2) bottle under nitrogen at −78 °C. After the addition, Et_3N–5HF was brought to room temperature and stored in a Teflon bottle with a tight cap at room temperature which will keep for a month without change. Et_3N–5HF is superior to commercially available Et_3N–3HF as the electrolyte for the electrochemical oxidation of organic compounds [45–52].

[2] Tetrafluoroethylene-perfluoroalkylvinyl-ether co-polymer.

[3] Recently, it has been reported that the methylene group located between the carbonyl group and sulfur atom in the compounds can be fluorinated by **1b** alone in CH_2Cl_2 [54,55].



Scheme 1. Reaction of β-ketoesters using **1b** in HF-base.

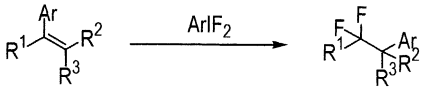


Scheme 2. Mechanism in the fluorination of β-ketoesters with **1b** in HF-base.

The mechanism in the fluorination of **2** with **1** is proposed as shown in Scheme 2. The attack of iodine atom (I) in molecule **1** activated by HF toward the enolate oxygen atom in **2b** initiates the reaction to produce intermediate **2A** accompanied by the elimination of HF. The subsequent elimination of ArI and fluoride ion from **2A** may take place affording products of diastereoisomers **3**(*S*) and **3**(*R*) accompanied by the concerted attack of another fluoride ion towards the α-position in **2A**. The bulkiness of the alkyl group (R^3) located at the alkoxy group (R^3O) in the ester functional group of **2A** may exert steric hindrance in the reaction. This steric effect determines the ratio of **3**(*S*) to **3**(*R*) in the products. As the conformation of the transition state can be illustrated as **2B** (Scheme 2), the substitution of a phenyl group in the chiral auxiliary phenylmethyl brings about the predominant formation of one of these isomers [56].

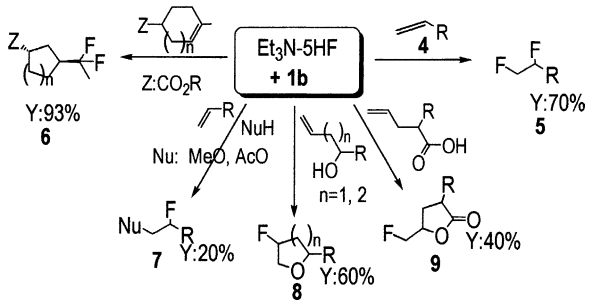
2.1.3. Fluorination of unsaturated bonds[4]

The reaction of arylgroup-substituted alkenes with **1** is known to produce *gem*-difluorocompounds with the migration of the aryl group (Eq. (6)) [40,60–64].



(6)

[4] For the fluorination of alkenes, F_2 and XeF_2 have been used to give simple 1,2-addition products. Their fluorination mechanism is different from that of ***1*** and they are known to generate highly reactive electrophilic fluorine sources [57–59], while ***1*** offers a stable fluoride ion in the fluorination of alkenes.



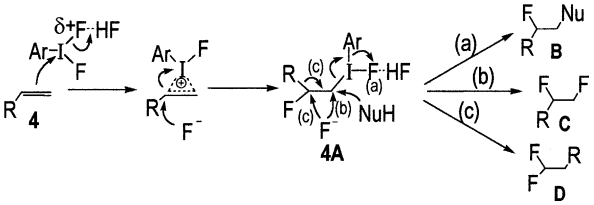
Scheme 3. Fluorination of alkenes with **1b** in Et_3N–5HF.

The selective fluorination of various unsaturated organic compounds with **1b** has been successfuly achieved in the presence of HF combined with a base (e.g. Et_3N–5HF) at room temperature for several 10 min (Scheme 3) [65,66]. Namely, in the presence of HF-base, the reaction of terminal alkenes **4** and a cycloalkene derivative with no substituents on its double bond with **1b** took place affording simple 1,2-addition products (*vic*-difluorocompounds) **5** without the carbon skeletal rearrangement of starting alkenes. A cyclohexene derivative produced a *cis*-adduct stereoselectively The ester, acetoxy, chloro, and even free hydroxy groups in the substrates did not react under the present conditions.

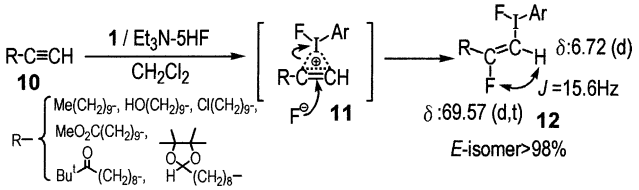
However, the reaction of internal alkenes other than cyclic alkenes was very slow and a complex mixture of products was obtained. On the other hand, the selective ring contraction and *gem*-difluorination of 4-alkyl-3-cyclohexene carboxylic esters took place to produce 3-(1′1′-difluoroalkyl)-cyclopentane derivatives **6**. Furthermore, an ester group and a difluoroalkyl group on the five-membered ring exclusively occupy the *trans* position [67]. When using Et_3N–5HF including nucleophiles such as ROH and AcOH, the reaction of alkenes with **1b** yields monofluorinated alkoxy or acetoxy compounds **7** [68]. Thus, for alcohols or carboxylic acids with a double bond at appropriate positions, fluorocyclization occurs to produce monofluorinated cyclic ethers **8** or lactones **9**, respectively.

The above reactions probably proceed as shown in Scheme 4.

HF-bases such as Et_3N–5HF seem to act as an acid catalyst to activate **1**, because the reaction did not occur without HF-base or with neutral Et_3N–3HF. The double bond of the alkene was attacked by **1** as activated by HF followed by the addition of a fluoride ion to produce the



Scheme 4. Mechnism of fluorination of terminal alkenes with **1**.



Scheme 5. Reaction of terminal alkynes with **1**.

unstable alkyl iodine(III) intermediate **4A**. The elimination of ArI from **4A** and another attack of fluoride ion or nucleophiles with or without the migration of alkyl groups occurred to provide products **B**, **C**, and **D**, respectively.

The reaction of terminal alkyne **10** with **1** in Et_3N–5HF yielded adducts **12** via intermediate **11** in high yields [69], which are sufficiently stable to isolate. Adducts **12** are characterized by their configuration being the same as that of [*E*]-2-fluoro-alk-1-enyl-4-aryl iodonium salt [70–74][5] from the coupling constant *J* between F and H, whose magnitude is 15 Hz and corresponds well to that of *trans*-formation (Scheme 5). Functional groups such as ester and hydroxyl groups in **10** did not affect the yields of **12** (Scheme 5). The adducts **12** were extracted using CH_2Cl_2 and used for further transformation without isolation (see Chapter 2.3).

2.1.4. Deiodofluorination of RI with $ArIF_2$

The oxidative fluorination of alkyl iodides (RI) **13** with **1** alone, such as methyl and bridgehead iodides [75], was reported to produce the corresponding alkyl fluorides (RF) **15** via reactive hypervalent alkyliodine difluoride intermediates, RIF_2 **14** under mild conditions (Eq. (7)) [76,77].

$$\underset{\mathbf{13}}{RI} \xrightarrow{XeF_2 \text{ or } ArIF_2} \underset{\mathbf{14}}{RIF_2} \longrightarrow \underset{\mathbf{15}}{RF} \tag{7}$$

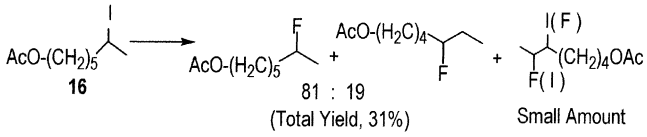
However, the application of this reaction to *prim*-alkyl iodides for the synthesis of the corresponding *prim*-alkyl fluorides resulted in a poor yield of **15** [78]. In the presence of HF-base, the oxidative fluorination of *prim*-alkyl iodides with **1b** successfully occurred to selectively provide corresponding *prim*-alkyl fluorides under mild conditions, as shown in Eq. (8) [79].

$$\underset{\mathbf{13}}{RI} \xrightarrow[Et_3N\text{-}4HF\ /\ CH_2Cl_2,\ rt.]{p\text{-Tol-IF2(1.3~1.5eq)}} \underset{\mathbf{15}}{RF} \tag{8}$$

In the presence of the neutral complex, Et_3N–3HF, the reaction of **13** with **1b** did not occur, but was markedly enhanced by the addition of a slightly acidic complex of Et_3N–4HF. The presence of more acidic complexes such as Et_3N–5HF decreased the yield of **15** with the formation of a

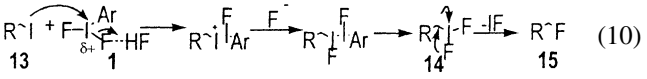
[5] (*Z*)-(2-Fluoroalk-1-enyl)(aryl)iodonium salts were previously prepared from (alk-1-ynyl)(aryl)-iodonium salts but in low yields [72]. More recently, we have developed the effective synthesis of (*Z*)-(2-fluoroalk-1-enyl)(aryl)iodonium by the reaction of **10** with **1b** in the presence of MeOH followed by a treatment with 30% aqueous $NaBF_4$ [73].

considerable amount of by-products. The highly chemoselective feature of this procedure was demonstrated in the reactions of **13** having a tosyl and a benzyl chloride groups to selectively give monofluorinated products.[6] On the other hand, *sec*-alkyl iodide yielded a complex mixture of products with the formation of a small amount of the desired *sec*-alkyl fluoride (Eq. (9)).



(9)

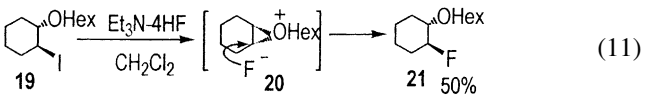
The reaction can be well described by Eq. (10).



(10)

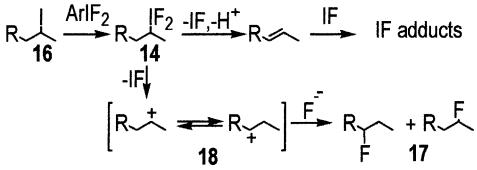
In the initial step of the reaction, unstable **14** may form by the ligand transfer from **1** to **13** and decompose to afford **15** through the subsequent attack by fluoride ion [76,77]. Since the reaction occurs regioselectively and the skeletal rearranged products of **15** do not form through the reaction of *prim*-alkyl iodides, the reaction proceeds via the S_N2 mechanism between **14** and the fluoride ion. For the successful conversion of *prim*-alkyl iodides to fluorides, the addition of a slightly acidic amine–HF complex is critical and the role of the amine–HF complex is more critical than that of the fluoride source. As described earlier, $ArIF_2$ (**1**) is activated by acids for the fluorination of organic compounds such as β-ketoesters, alkenes, and alkynes. For the deiodofluorination of RI, the Et_3N–4HF complex may also properly activate **1** by coordination. However, highly acidic complexes such as Et_3N–5HF may act towards **14** to decompose it drastically forming a considerable amount of undesirable products. On the other hand, neutral Et_3N–3HF cannot activate **1** by coordination, moreover, free Et_3N existing in Et_3N–3HF may react with **13** and prevent the formation of **14**. On the other hand, a considerable amount of isomers **17** of RF was formed in the reaction of *sec*-alkyl iodides **16**, which may involve the carbonium ion intermediate **18** as shown in Scheme 6.

The reaction of *trans*-2-alkoxyiodocyclohexane (**19**) with **1b** afforded *trans*-2-alkoxyfluorocyclohexane (**21**) in moderate yields. As the *trans*-stereochemistry of **19** was completely kept in **21**, the reaction must be occurring through an oxonium intermediate **20** (Eq. (11)) [80].



(11)

[6] Such selectivity could not be observed in the conventional S_N2 halogen-exchange fluorination reactions of alkyl halides using KF.



Scheme 6. Mechanism of fluorination of *sec*-alkyl iodides with **1**.

2.2. Iodine pentafluoride (IF_5)

2.2.1. Novel fluorination reagent: IF_5/Et_3N–3HF

Iodine pentafluoride (**22**) itself is a very hazardous chemical (bp: 100.5 °C, mp: 9.4 °C, p 2.19 × 10^3 Pa at 21 °C) and extremely sensitive to moisture [81]. Most organic compounds readily carbonize on contact with **22**, sometimes with confiagration, except for perfluorinated ones [25,82–86].[7] In contrast, a solution of **22** in Et_3N–3HF (IF_5/Et_3N–3HF (IF_5:Et_3N:HF = 1:1:3 molar ratio)) is easy to prepare[8] and is not sensitive to moisture. And IF_5/Et_3N–3HF is a stable solution with a low vapor pressure of p 0.27 × 10^3 Pa at 21 °C,[9] it is not hazardous to handle and does not require any particular precautionary measures. In addition, this solution exerts a powerful and selective fluorination ability for various organic compounds having a C–H bond without the need for custom-made equipment [87]. Representative results are shown in Table 1.

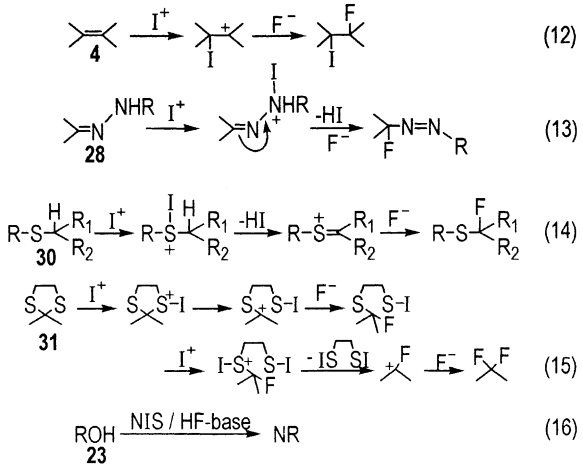
Although Et_3N–3HF itself cannot initiate the fluorination of alcohol and epoxide under the conditions shown in Table 1, the transformation of alcohols **23** to alkyl fluoride, including *prim*-alcohols, the preparation of acyl fluoride from carboxylic acids **24** and the fluorinative ring-opening of epoxides **25** can be accomplished readily by IF_5/Et_3N–3HF. The fluorination also occurs at the carbon atom in the carbonyl group **26** and its derivatives such as hidrarones **27**–**29** and thio-ketals **32** to produce difluorinated products. In case of thio-acetal **32**, difluorination selectively occurs at carbon atom located next to the carbonyl carbon. The sulfur atom in substrates such as thio-ethers **30** and **34** enhances the fluorination of C–H bonds in the neighboring alkyl groups resulting in the formation of the corresponding difluorinated products. On the other hand, the reaction of alkene **4** and alkyne **10** with this reagent does not occur.

Incidentally, as shown in Scheme 7, in a similar way to using the IF_5/Et_3N–3HF reagent, a combined reagent system consisting of fluoride ion (F^-) and iodonium ion (I^+), such as *N*-iodosuccinimide/HF-molten salt, reacts with **28**, **30**,

[7] IF_5 is industrially produced for the production of surfactant and textile chemicals [25,83,94].

[8] A prescribed amount of Et_3N–3HF was pipetted into 50–100 mmol of IF_5 in a 30 ml PFA bottle without cooling since the temperature did not rise appreciably. Thus, particular precautionary measures are not necessary for the preparation of IF_5/Et_3N–3HF. This reagent can be stored in a PFA bottle for several month on a laboratory table without taking precautionary measures and without any deterioration of fluorination activity.

[9] Vapor pressure measurement of IF_5/Et_3N–3HF was carried out according to the technique in [86].



Scheme 7. Fluorination mechanism of organic compounds using NIS/HF-molten salt.

and **31** to afford the corresponding fluorinated products (Eqs. (13)–(15)).

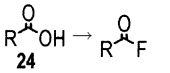
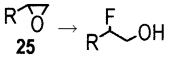
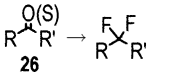
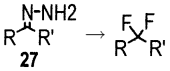
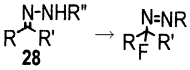
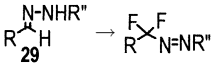
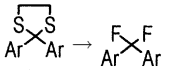
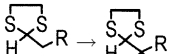
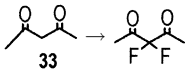
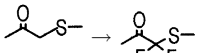
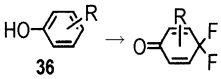
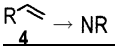
The reaction of this combined reagent with alcohol, however, does not take place (Eq. (16)), but the iodofluorination of alkenes **4** with this reagent occurs readily to afford corresponding fluorides (Eq. (12)). Thus, the notable difference in reactivity between NIS/HF-base and IF_5/Et_3N–3HF is observed for the fluorination of simple alkenes (Eq. (12)) and alcohols (Eq. (16)). The ion pair of I^+F^- generated in this combined reagent can play an important role in these reactions. Thus, the mechanism of fuorination using IF_5/Et_3N–3HF may be different from that using NIS/HF-molten salt reagent.[10]

As shown in Fig. 1, in the ^{19}F NMR spectrum two signals (50.2 and 10.1 ppm), corresponding to two kinds of fluorine atom in IF_5 become extinct in the IF_5/Et_3N–3HF solution, and a new chemical shift is observed at −53.1 ppm as a broad singlet. Judging from these NMR observations, **22** in the Et_3N–3HF solution may form a novel complex.

The structure of the complex has not been confirmed yet, but it may be $IF_4^+[Et_3NH^+HF_2^-]HF_2^-$ or $IF_6^-[Et_3NH$–$2HF]^+$ since the signal for the ammonio group (Et_3NH^+) is clearly seen in the ^1H NMR spectrum of this solution. Although no report appears in the literature on the reaction of IF_5 in HF-molten salts such as Et_3N–3HF, there are some reports on the behavior of IF_5 without or with acids (such as HF and SbF_5) and salts (such as Me_4NF and KF) to form IF_4^+ and/or IF_6 [88–90]. However, as shown in Scheme 8 [91], it is difficult to form ion pairs such as $IF_4^+F^-$ (or IF_6^-) in molecule **22**, because of its thermodynamically unfavorable self-dissociation.

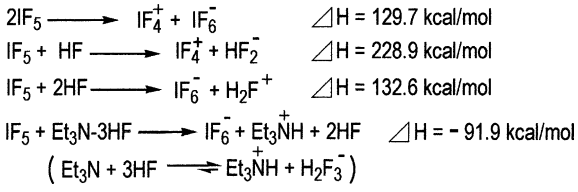
[10] We have contributed the results in the fluorination using IF_5/Et_3N–3HF as a novel fluorination reagent to Chem. Commun. J. However, two of three referees insisted strongly that IF_5–Et_3N–3HF is not a new fluorination system but is that of the familiar I^+/F^- type and they judged our manuscript inappropriate for the journal. To our regret, the journal has rejected our manuscript for publication.

Table 1
Fluorination of various organic compounds using IF_5/Et_3N–3HF

Substrate → product	Yield (%)
ROH → R–F (23)	90
 (24)	75
 (25)	75
 (26)	80
 (27)	70
 (28)	78
 (29)	55
$ArS-CH_3 \rightarrow ArS-CHF_2$ (30)	50
 (31)	95
 (32)	60
 (33)	71
 (34)	85
Ar-NHNH$_2$ → Ar-F (35)	30
 (36)	53
 (4)	

Conditions: IF_5/Substrate = 1.1 mola ratio; Temp. rt ∼ 100 °C, mostly, Rt; Time, 0.5–24 h, generally, 0.5–1 h; Solvent, Heptane, Hexane, CH_2Cl_2 or none.

The formation of IF_4^+ and IF_6^- in IF_5 solution in HF is also unfavorable thermodynamicatly. However, the formation of IF_6^- in IF_5 solution in Et_3N–3HF is favorable thermodynamically. Also, the structure of IF_6^- formed by the addition of Me_4NF or KF to IF_5 has been confirmed by X-ray analysis [92]. In addition, by taking the ratios of



Scheme 8. Activation enthalpy for formation of IF_4^+ and IF_6^-.

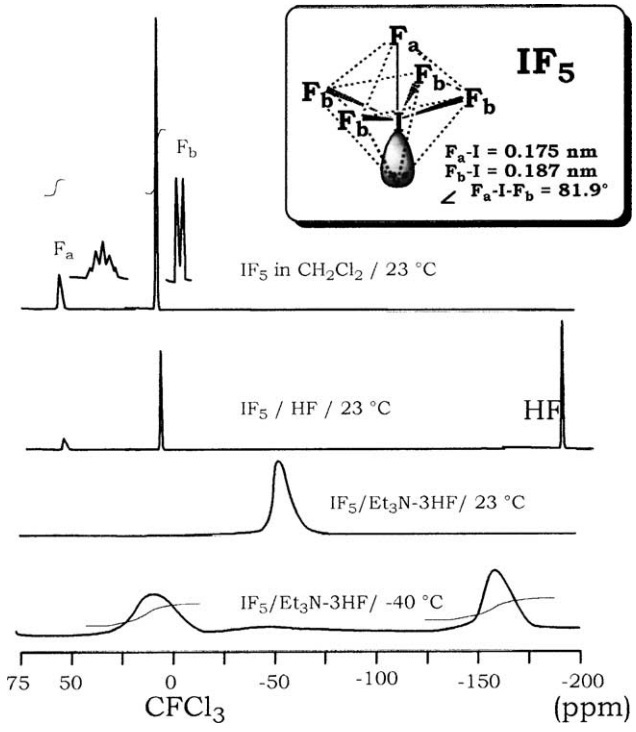


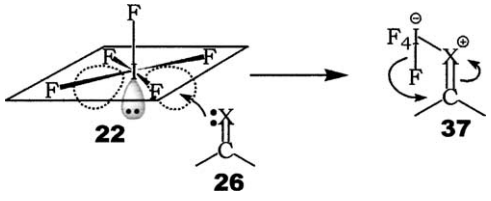
Fig. 1. ^{19}F NMR spectra of IF_5, IF_5/HF, and IF_5/Et_3N–3HF.

the vapor pressure of IF_5:100 and Et_3N–3HF:1 to that of IF_5/Et_3N–3HF:10 into consideration, it may be reasonable to consider the equilibration between IF_5 and IF_6^- species in the IF_5/Et_3N–3HF solution (Eq. (17)).

$$IF_5 + Et_3N{-}3HF \rightleftharpoons Et_3\overset{+}{N}H + IF_6^- + 2HF \quad (17)$$

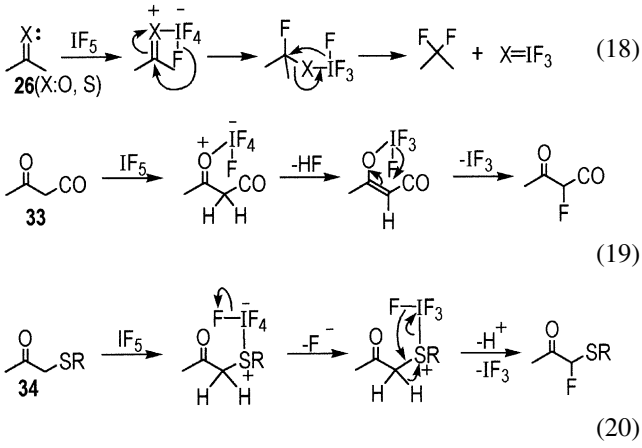
Based on the considerations mentioned above, the Lewis acidity of **22**, which equilibrated with IF_6^- may play an important role in the fluorination of organic compounds with IF_5/Et_3N–3HF. Thus, as shown in Scheme 9, heteroatoms such as oxygen in the carbonyl group **26** may coordinate with the vacant orbital of iodine in the IF_5 molecule forming oxonium salt **37**.

Moreover, intramolecular nucleophilic fluorination may take place affording a *gem*-difluorinated product (Eq. (18)). The fluorination of the methylene group located between two carbonyl groups **33** or between carbonyl and a sulfur atom in substrate **34** may also be initiated by the coordination of IF_5 to a carbonyl oxygen and/or sulfur atom. Then, intramolecular nucleophilic fluorination takes place to give



Scheme 9. Coordination of carbonyl group with **22**.

the fluorinated products by eliminating HF and IF_3 (Eqs. (19) and (20)).

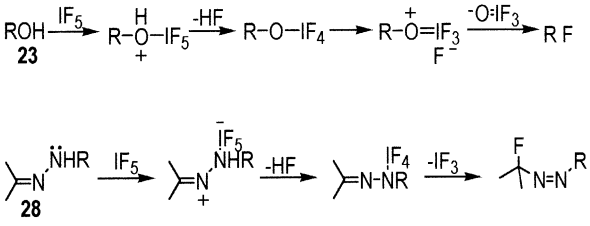


(18)

(19)

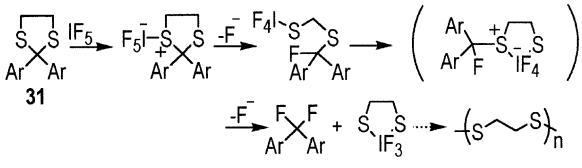
(20)

The dehydroxy-fluorination of alcohol **23** affords the corresponding alkyl fluoride accompanying with elimination of O=IF_3 (Eq. (21)). The mechanism of the fluorination of *N*-substituted hydrazone **28**, diaryl-thioketal **31**, and thioacetal **32** with IF_5 is also well elucidated in similar ways as shown in Eqs. (22) and (23), and Scheme 10, respectively.

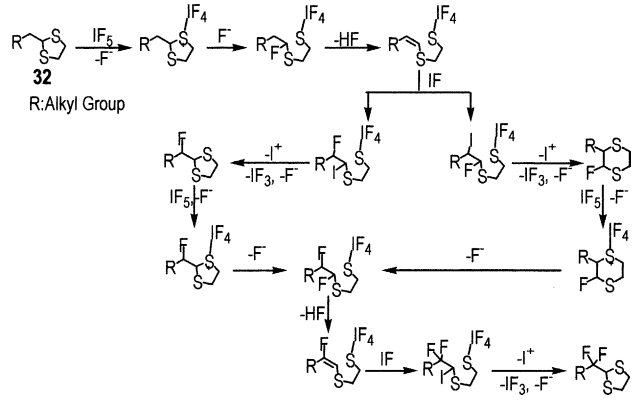


(21)

(22)



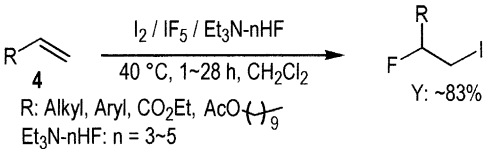
(23)



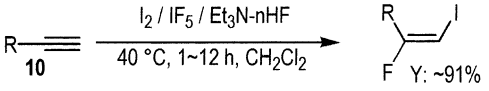
Scheme 10. Mechanism of fluorination of thioacetals **32** with IF_5/Et_3N–3HF.

2.2.2. Iodofluorination with IF_5/Et_3N–3HF in the presence of iodine

The reactions of alkenes and alkynes with IF_5/Et_3N–3HF dose not occur. However, in the presence of I_2, the iodofluorination of terminal alkenes **4** and alkynes **10** with IF_5/Et_3N–3HF occurs readily producing the corresponding iodo-alkyl fluoride and α-fluoro alkenyl iodide in good yields (Eqs. (24) and (25)).



(24)

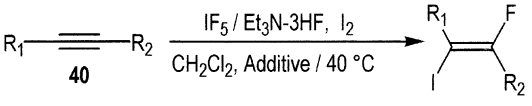


(25)

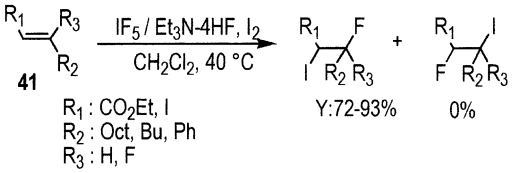
The reaction of perfluoro-alkenes such as tetrafluoro ethene (**38**) with an I_2 solution in IF_5 produces perfluoroethyl iodide (**39**). This reaction is employed industrially for the production of surfactants and textile chemicals (Eq. (26)).[7]

$$\underset{\mathbf{38}}{CF_2{=}CF_2} \xrightarrow[Al/AlI_3,\,22\,^\circ C,\,15\,h]{IF_5+2I_2} \underset{\mathbf{39}}{CF_3{-}CF_2I} \qquad (26)$$

However, the I_2/IF_5 solution without HF-base exhibits a very high reactivity for **4** and **10** to form a considerable amount of tar-like matter, while the I_2 solution in Et_3N–3HF has no reactivity for these unsaturated compounds. The iodofluorination of internal alkynes **40** and alkenes **41** occurs with high regioselectivity (Eqs. (27) and (28)). The active species in this reaction may be the "IF" formed in the reaction between IF_5 and I_2 (Eq. (29)).



(27)



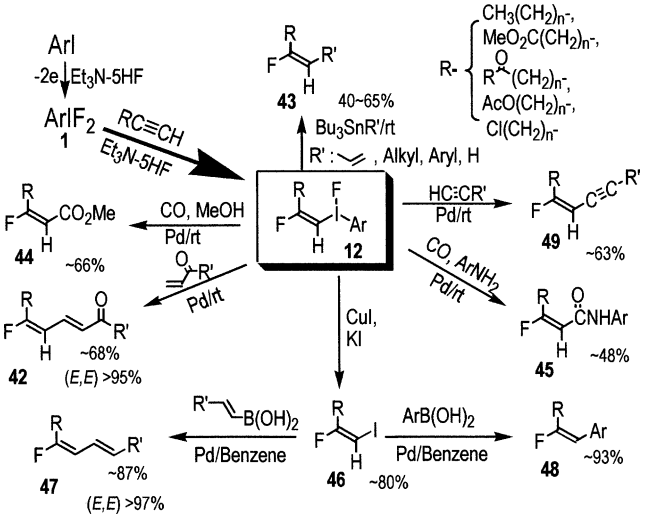
(28)

$$IF_5 + 2I_2 \rightarrow 5IF \qquad (29)$$

2.3. (E)-2-Fluoro-alk-1-enyl-4-aryl iodonium salts

The stereo and regioselective synthesis of (*E*)-α-fluoro-β-substituted alkene analogs has been successfully achieved by using (*E*)-2-fluor-alk-1-enyl-4-aryl iodonium salts (**12**) (Scheme 11) [93].

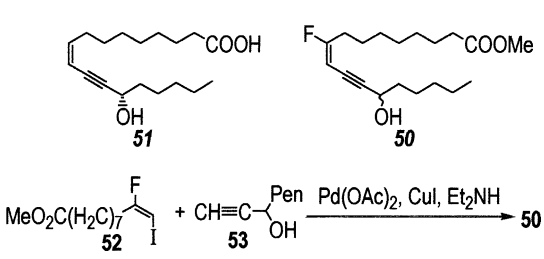
The reaction of α,β-unsaturated conjugated carbonyl compounds with **12** yields δ-fluoro-α,β,γ,δ-unsaturated carbonyl compounds **42** in highly stereoselective yields in the presence of a Pd catalyst [94]. The palladium-catalyzed



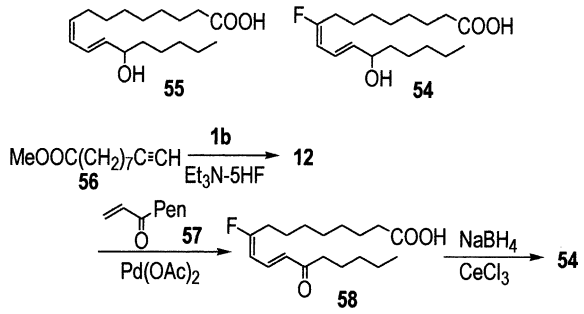
Scheme 11. Stereo- and regioselective synthesis of (*E*)-α-fluoro-β-susbstituted alkenes.

cross-coupling reaction of **12** with organotin compounds such as vinyl, alkyl, aryl and hydride butyltins also succeeded in producing α-fluoro-α,β-conjugated dienes (**43**) in moderate to good yields stereoseiectively at room temperature [94]. In a similar way, the carbonylatlon of **12** with carbon monoxide affords corresponding 2-fluoro-α,β-unsaturated esters **44** [95]. Also, the carboxyamination of **12** with amino compounds takes place producing corresponding α-fluornalkenyl amido compounds **45** stereoselectively. The iodonation of **12** by modifying the previously reported procedure [96,97] yielded the (*E*)-isomer of 2-fluoro-1-iodoalk-1-enes (**46**) in good yields [69]. The coupling reaction of **46** with organoboronic acid can take place efficiently to produce the (*E*)-isomer of fluoro-alkenes **47** and **48** selectively in high yields under mild conditions [98–101]. These reactions can be carried out without the protection of functionalities in the substrate **12** such as ketones, esters, and even hydroxy groups.

The methodology for the preparation of α-fluoroalkenes is interesting from the viewpoint of the introduction of a fluorine atom into the double bond of natural products with pharmacological properties different from those of the original compounds. For example, the [±]-9-fluorodehydrocoriolic acid (**50**) may be synthesized by the reaction of methyl (*E*)-10-iodo-9-fluoro-9-decenoate (**52**), prepared from methyl-9-decynoate, with 1-octyn-3-ol (**53**) in the



Scheme 12. Synthesis of [±]-9-fluorodehydrocoriolic acid.



Scheme 13. Synthesis of β-fluoro 13 HODE.

presence of a Pd catatyst and CuI (Scheme 12), which is the fluorinated analog of the 11,12-dehydrocoriolic acid (**51**) having stronger inhibitory activity than the natural coriolic acid against rice blast fungus [101].

Another example is the synthesis of the fluorinated analog **54** of (9*Z*,11*E*)-13-hydroxy-9,11-octadecadienoic acid (13 HODE) (**55**) [102], which may have interesting bioactivities [103] and have attracted the attention of both chemists and biochemists (Scheme 13) [98]. Methyl-9-decynoate (**56**) was reacted with **1b** in the presence of Et_3N–5HF at room temperature and the resulting fluoroalkenyliodonium salt was used for the Heck-type reaction with 1-octen-3-one (**57**) to give methyl-(9*Z*,11*E*)-13-hydroxy-9,11-octadecadienoate (**58**) in 55% overall yield from **56**. The reduction of the keto-function of **57** provided the desired 9-fluoro 13 HODE (**54**).

3. Electrochemical fluorination involving iodine compounds

3.1. Electrochemical deiodofluorination of alkyl iodides

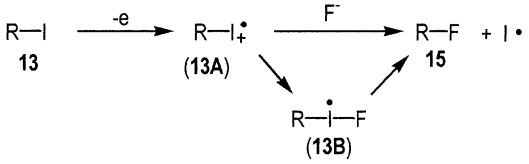
The electrochemical oxidation of RI **13** using Et_3N–*n*HF as an electrolyte yields RF **15** under a constant potential (Eq. (30)) [104,105].

$$\underset{\mathbf{13}}{R\text{–}I} \xrightarrow[Et_3N-3HF/solvent]{-e/RT,\ 2.0\text{–}2.5\ V(\text{versus Ag/Ag}^+)} \underset{\mathbf{15}}{R\text{–}F} \tag{30}$$

The reaction took place effectively in the presence of Et_3N–3HF as an electrolyte affording **15** in high yields. When using Et_3N–5HF as an electrolyte, on the other hand, the yields of **15** were decreased with the formation of a significant amount of by-products due to its strong acidity. Since the iodine atom of RI has a lower oxidation potential than those of other functional groups such as ketone, ester, chloro and tosylate, the reaction proceeds with high chemoselectivity under a controlled potential at which only the iodine atoms in the substrate are selectively oxidized [106].[11]

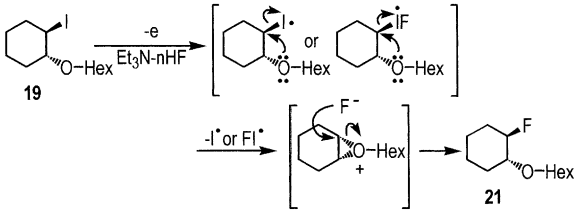
[11] The excess electricity may be consumed to oxidize the liberated I or I_2 [107].

The reaction has been elucidated to be initiated by the one-electron oxidation of **13** to form its cation radical (**13A**) (Eq. (31)).



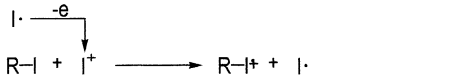
(31)

As *sec*-alkyl fluorides do not form in the reaction of *prim*-alkyl iodides, an S_N2-like path may be postulated for the further reaction of cation radical intermediates with fluoride ion to produce **15** via radical intermediates (**13B**). A specific example is the reaction of **19**, whose alkoxy group was substituted at the neighboring carbon, to afford the corresponding *sec*-alkyl fluoride **21** in reasonable yields and the *trans*-stereochemistry of **19** was maintained in the product (Eq. (32)).

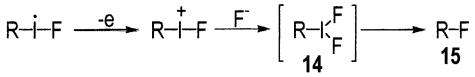


(32)

One cannot rule out the possibility of indirect oxidation of RI with electrogenerated I^+, and/or the formation of difluoro-iodo alkanes (hypervalent iodan) intermediate **14** path (Eqs. (33) and (34)).

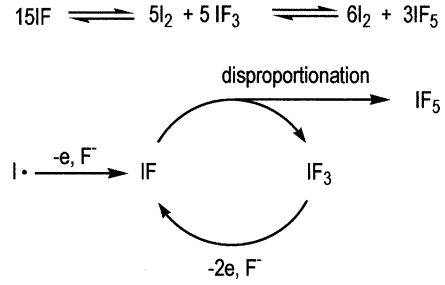


(33)



(34)

In order to complete the electrochemical deiodofluorination of **13**, an excess amount of electricity (6–7 F/mol) was needed for the conversion of **13** to the corresponding **15**. The excess electricity may be consumed for the oxidation of the liberated iodine radical (**I•**). Namely "IF" species may be formed by the further one-electron oxidation of the initially



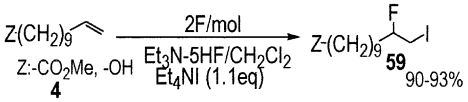
Scheme 14. Electrochemical oxidation–disproportionation sequence of I radical in HF-base.

formed $I^{\bullet}$·and its subsequent fluorination with a fluoride ion. IF_5, thus formed, can disproportionate to IF_3, IF_5 and I_2 in the solution (Scheme 14).

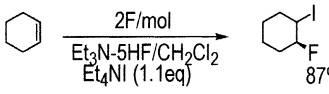
Thus, the two-electron oxidation of I_2 generates IF, which then disproportionates to IF_5 and I_2 [84]. The oxidation–disproportionation sequence continues until all $I^{\bullet}$ is converted to IF_5 during the reaction and 5 F/mol of electricity is necessary to oxidize all the liberated $I^{\bullet}$.

3.2. Iodofluorination of unsaturated bonds with electrochemically generated iodonium ion in HF-base

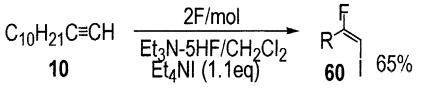
The iodofluorination of **4** (including cyclohexene derivatives) and **10** has been successfully carried out using electrochemically generated iodonium ion (I^+) from a variety of iodide anion sources in the CH_2Cl_2 in Et_3N–5HF electrolyte under a constant potential (1.2–1.5 V (versus Ag/Ag^+)) at room temperature to yield iodofluorination products **59** and **60** (Eqs. (35)–(37)).



(35)



(36)



(37)

When Ph_4PI, I_2, or LiI was used as an iodide ion source, passivation on the anode took place predominantly. On the other hand, Et_4NI and NaI were suitable for generating iodonium cation to afford iodofluorinated products with high regioselectivity (>98%) in good yields with a high current efficiency. Moreover, the presence of functionalities such as hydroxy and ester groups in the substrate **4** did not disturb the desired reaction. Interestingly, (*E*)-2-fluoro-1-iodo-1-alkene (**60**), which is difficult to obtain by a previously reported procedure [108], was produced stereo- and regioselectively using the electrochemically generated iodonium cation. The reaction probably initiated by the two-electron oxidation of iodide anion to form I^+ is shown in Eq. (38).

$$I^- \xrightarrow{-e} I^{\bullet} \xrightarrow{-e} I^+ \quad (38)$$

Thus, the anodic oxidation of iodonium compounds such as Et_4NI may be essential for the generation of "IF" in the iodofluorination of **4** and **10**. The reaction was carried out using a divided cell, where the reduction of intermediate iodonium cation may take place in the cathode compartment so that the current efficiency is sufficiently high compared with that of the reaction using an undivided cell. The double bond of an alkene reacts with the highly reactive iodonium cation I^+ yielding an iodonium intermediate following the addition of a fluoride ion according to Markovnikov's rule, thereby producing the corresponding iodofluoroalkanes. The procedures for the iodofluorination of carbon–carbon unsaturated bonds reported so far required inaccessible reagents such as I_2, NIS, IF ($I_2 + F_2$), I (pyridine)$_2BF_4$, and I (collidine)$_2BF_4$ for the iodonium cation (I^+) source, as described in Section 1. Compared to these procedures, electrochemically generated I^+ comes from readily available chemicals such as Et_4NI and NaI with an economical advantage.

4. Conclusions

A wide variety of reagents have been developed for introducing fluorine into organic compounds over the last 50 years [109]. For the last half decade, we have explored novel methoodlogies for the preparation of fluorine-containing organic compounds making use of the unique properties of iodine, especially its hypervalency (trivalent and pentavalent) states. In addition, the electrochemical selective iodo-exchange fluorination of alkyl iodides has been performed with high chemoselectivity to produce corresponding alkyl fluorides. Moreover, the economically advantageous iodofluorination procedure of carbon–carbon unsaturated bonds compared with the thus far well-studied large number of conventional iodofluorination procedures has been demonstrated using electrochemically generated iodonium cation which can be generated from readily available, inexpensive iodo-compounds such as Et_4NI and NaI.

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[12] The author would like to strongly protest Hara's, the corresponding author of [105], exclusion of Yoneda's name from the author's list in [105], which has similar contents to those of [104]. Incidentally, Hara has contributed these [98,99,101] without Yoneda's consent.

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