



Oxidative fluorination with Selectfluor: A convenient procedure for preparing hypervalent iodine(V) fluorides

Samuel M. G. Dearman¹, Xiang Li², Yang Li², Kuldip Singh¹ and Alison M. Stuart^{*1}

Full Research Paper

Open Access

Address:

¹School of Chemistry, University of Leicester, Leicester, LE1 7RH, UK and ²School of Chemical Engineering, Dalian University of Technology, No. 2 Linggong Road, Dalian, 116024, P. R. China

Email:

Alison M. Stuart* - Alison.Stuart@le.ac.uk

* Corresponding author

Keywords:

fluorination; fluorobenziodoxoles; halogen bonding; hypervalent iodine; Selectfluor

Beilstein J. Org. Chem. **2024**, *20*, 1785–1793.

<https://doi.org/10.3762/bjoc.20.157>

Received: 30 April 2024

Accepted: 03 July 2024

Published: 29 July 2024

This article is part of the thematic issue "Hypervalent halogen chemistry".

Guest Editor: T. Gulder



© 2024 Dearman et al.; licensee Beilstein-Institut.
License and terms: see end of document.

Abstract

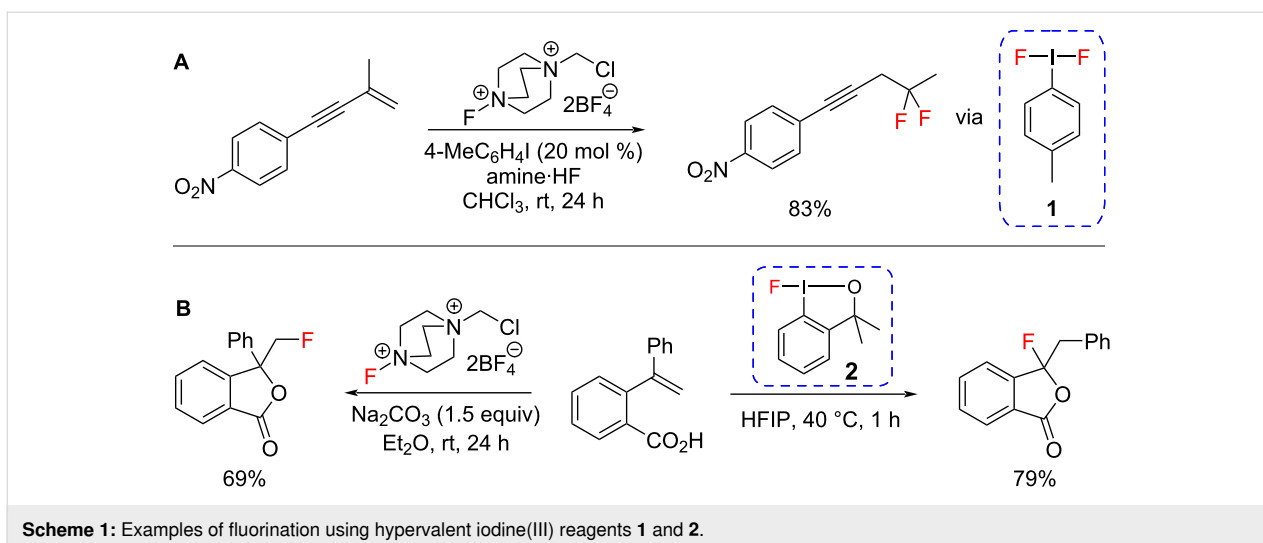
The ability to investigate hypervalent iodine(V) fluorides has been limited primarily by their difficult preparation traditionally using harsh fluorinating reagents such as trifluoromethyl hypofluorite and bromine trifluoride. Here, we report a mild and efficient route using Selectfluor to deliver hypervalent iodine(V) fluorides in good isolated yields (72–90%). Stability studies revealed that bicyclic difluoro(aryl)- λ^5 -iodane **6** was much more stable in acetonitrile- d_3 than in chloroform- d_1 , presumably due to acetonitrile coordinating to the iodine(V) centre and stabilising it via halogen bonding.

Introduction

An important strategy in the drug discovery process is the incorporation of fluorine into biologically active molecules because fluorine can improve bioactivity and pharmacokinetic properties [1]. Consequently, 22% of all small-molecule drugs contain at least one fluorine atom [2]. Hypervalent iodine(III) fluorides, such as difluoroiodotoluene **1** and fluoroiodane **2**, have been key to the development of numerous, new synthetic procedures for C–F bond formation over the last decade. Since difluoroiodotoluene **1** has low chemical stability and is highly hygroscopic, it is often prepared in situ and Gilmour [3–8] has reported a range of fluorination protocols utilising hypervalent

iodine(I/III) catalysis (Scheme 1A). Lennox has also demonstrated that **1** can be generated cleanly by electrochemical oxidation [9,10]. In an alternative approach, we reported the first application of using fluoroiodane **2** as a fluorinating reagent in 2013 [11]. The chelate sidearm makes **2** an air-stable, easy-to-handle solid with excellent fluorinating ability and it often exhibits different reactivity to that observed with fluoroaza reagents such as Selectfluor (Scheme 1B) [12–20].

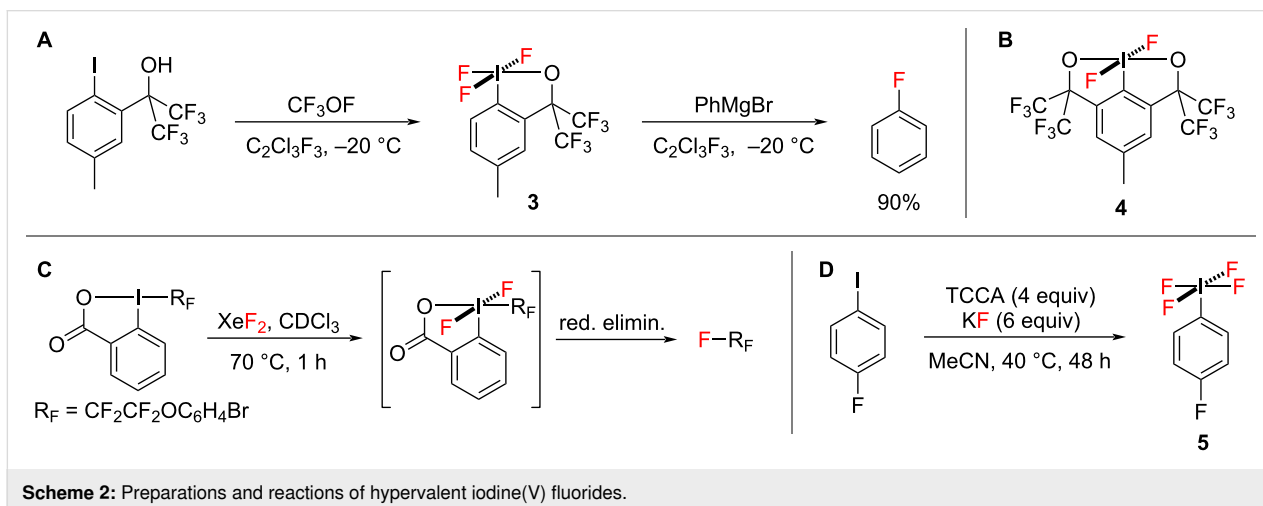
In contrast to the chemistry of hypervalent iodine(III) reagents, very little is known about hypervalent iodine(V) fluorides. One



problem that has blocked research into these compounds has been the lack of synthetic procedures to access them easily because they normally require harsh fluorinating reagents. The synthesis of hypervalent iodine(V) fluoride **3** was reported by Amey and Martin in 1979 using the highly toxic gas, trifluoromethyl hypofluorite (Scheme 2A), and they later prepared bicyclic hypervalent iodine(V) fluoride **4** using bromine trifluoride (Scheme 2B) [21,22]. They also showed that hypervalent iodine(V) fluoride **3** fluorinated phenylmagnesium bromide in Freon-113 to form fluorobenzene in 90% yield (Scheme 2A) and so, it is very surprising that this reagent has not been investigated further. Since then, Gruber [23] reacted a perfluorinated iodine(III) compound with XeF₂ and postulated the formation of a (perfluoroalkyl)iodine(V) difluoride intermediate which underwent a reductive elimination to afford perfluorinated products (Scheme 2C). In 2019 Togni reported a safer route to a range of acyclic iodine(V) fluorides such as **5** (Scheme 2D) using large excesses of trichloroisocyanuric acid (TCCA) and

potassium fluoride [24]. The iodine(V) fluorides were formed in good spectroscopic yields (79–94%), but only one product, tetrafluoro(4-fluorophenyl)-λ⁵-iodane **5**, was isolated from the reaction mixture by performing multiple extractions into hexane under a nitrogen atmosphere in a glovebox. A similar synthetic approach to acyclic iodine(V) fluorides was developed more recently by Ismalaj and co-workers by reacting iodoarenes with 6 equivalents of KF and ex situ-generated chlorine gas within a two-chamber reactor setup, but again the iodine(V) fluorides were not isolated [25].

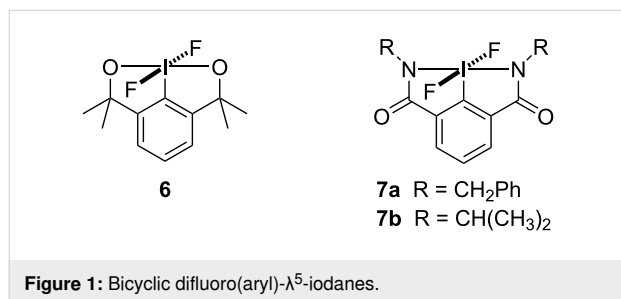
We became interested in developing a convenient procedure to access these intriguing reagents and to investigate their ability to fluorinate aryl Grignard reagents. In this paper, we report a straightforward route to hypervalent iodine(V) fluorides by reacting iodine(III) precursors with commercially available Selectfluor. The method avoids large excesses of reagents and pure iodine(V) fluorides are isolated after a simple work-up.



Results and Discussion

Preparation of bicyclic difluoro(aryl)- λ^5 -iodanes

Two different types of bicyclic difluoro(aryl)- λ^5 -iodanes were designed originally because of the stabilisation afforded from two five-membered rings (Figure 1). We started our investigation with bicyclic difluoro(aryl)- λ^5 -iodane **6**, building on the hypervalent iodine core skeleton used in fluoroiodane **2**, with an additional 5-membered ring to stabilise the iodine(V) centre. Both sidearms were also changed to amides because the NR group is a point of diversity which could be used to modulate the sterics and electronics of these novel hypervalent iodine(V) compounds.



Initially, we applied Togni's oxidative fluorination protocol to iodine(I) precursor **8** (Table 1). Reacting **8** with 4 equivalents of trichloroisocyanuric acid (TCCA) and 6 equivalents of potassium fluoride in dry acetonitrile at 40 °C for 48 hours formed difluoroiodane **6** in a 90% spectroscopic yield (Table 1, entry 1). An iodosyl decomposition product **9** was also formed during the work-up procedure in air. When the reaction time was short-

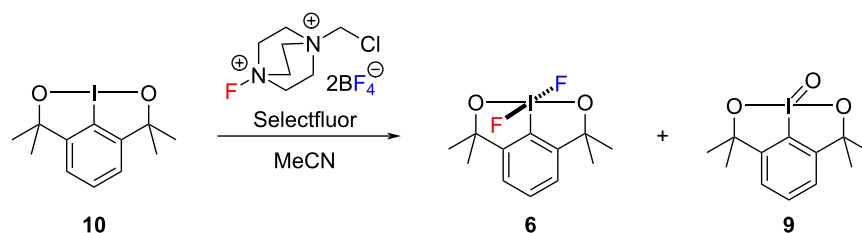
ened to 24 hours, a complex reaction mixture was obtained (Table 1, entry 2). Reducing the amount of TCCA to 3 equivalents (Table 1, entry 3) delivered difluoroiodane **6** in the same 90% yield. Finally, we performed the reaction and work-up under inert conditions and an excellent 99% yield of difluoroiodane **6** was achieved. The main issue with this procedure, however, was that we could not extract the pure difluoroiodane **6** into hexane and separate it from the large excesses of TCCA. Selectfluor was therefore explored as an oxidative fluorinating reagent (Table 1, entry 5). When **8** was reacted with 4 equivalents of freeze-dried Selectfluor in dry acetonitrile at 40 °C for 48 hours, difluoroiodane **6** was formed in 85% spectroscopic yield. However, the iodosyl decomposition product **9** was also produced in 15% spectroscopic yield, despite working the reaction up under inert conditions.

Consequently, we decided to investigate the oxidative fluorination of iodine(III) substrate **10** with Selectfluor (Table 2). We were delighted that difluoroiodane **6** was formed in 93% spectroscopic yield and the iodosyl byproduct **9** was formed in a much lower 7% spectroscopic yield, when **10** was reacted with a large excess of Selectfluor (5.1 equivalents) in dry acetonitrile at 40 °C for 48 hours (Table 2, entry 1). More importantly, difluoroiodane **6** was isolated successfully in an excellent 91% yield by a simple extraction into dry dichloromethane providing an efficient separation from the excess Selectfluor and its byproduct. Reducing the amount of Selectfluor to 2.5 equivalents and the reaction time to 24 hours (Table 2, entry 2) resulted in a similar high yield of difluoroiodane **6**. The reaction also proceeded well at either room temperature for 24 hours (Table 2, entry 3) or at 40 °C for 6 hours (Table 2, entry 4). Finally, reducing the amount of Selectfluor to 1.5 equivalents

Table 1: Oxidative fluorination of iodine(I) substrate **8**.

Entry	Reaction conditions	Time (h)	Yield ^a	
			6 (%)	9 (%)
1	TCCA (4 equiv), KF (6 equiv)	48	90	10
2	TCCA (4 equiv), KF (6 equiv)	24	complex mixture	
3	TCCA (3 equiv), KF (6 equiv)	48	90	10
4	TCCA (3 equiv), KF (6 equiv), work-up under N ₂	48	99	1
5	Selectfluor (4 equiv), work-up under N ₂	48	85 (56)	15

^aYield calculated by ¹H NMR spectroscopy, isolated yield shown in parenthesis.

Table 2: Oxidative fluorination with Selectfluor^a.

Entry	Selectfluor (equiv)	Temp. (°C)	Time (h)	Conversion (%)	Yield ^b	
					6 (%)	9 (%)
1	5.1	40	48	100	93 (91)	7
2	2.5	40	24	100	98 (80)	2
3	2.5	25	24	97	98 (58)	2
4	2.5	40	6	99	95 (55)	5
5	1.5	40	24	99	96 (90)	4

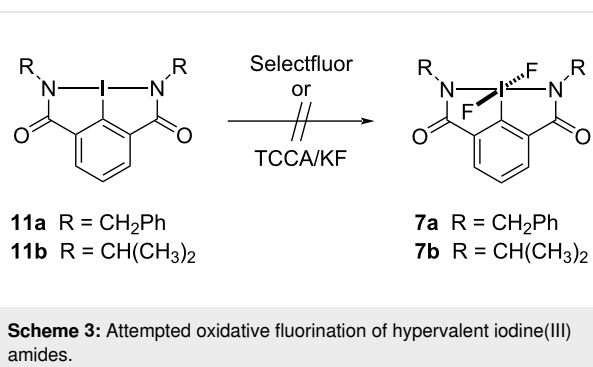
^aAll reactions performed in dry acetonitrile with freeze-dried Selectfluor under nitrogen and work-ups performed in dry solvents under nitrogen; ^bYield calculated by ¹H NMR spectroscopy, isolated yield shown in parenthesis.

led to an excellent 90% isolated yield and the conclusion that Selectfluor delivered one electrophilic fluorine (from the N–F) and one nucleophilic fluoride (from the tetrafluoroborate, BF₄⁻) to form difluoroiodane **6**.

The formation of difluoroiodane **6** was identified by a singlet at –23.0 ppm in the ¹⁹F NMR spectrum. As expected, the aromatic signals in the ¹H NMR spectrum shifted downfield from a doublet at 7.21 ppm and a triplet at 7.56 ppm for iodine(III) substrate **10** to 7.71 ppm and 7.96 ppm, respectively, for iodine(V) product **6**. Similarly, the ¹³C NMR spectrum showed a major downfield shift for the aromatic carbon attached to iodine from a chemical shift of 105.3 ppm in iodine(III) substrate **10** to 132.4 ppm for difluoroiodane(V) product **6**.

Since Selectfluor was shown to be the best reagent for preparing bicyclic iodine(V) difluoride **6**, this route was first investigated for the oxidative fluorinations of hypervalent iodine(III) amides **11a** and **11b** (Scheme 3). Unfortunately, these reactions did not work and difluoro(aryl)-λ⁵-iodanes **7a** and **7b** were not produced. Togni's protocol using TCCA (4 equivalents) and KF (6 equivalents) was then applied to both bicyclic iodine(III) amides **11a** and **11b**, but these reactions also failed to form either difluoroiodane **7a** or **7b**.

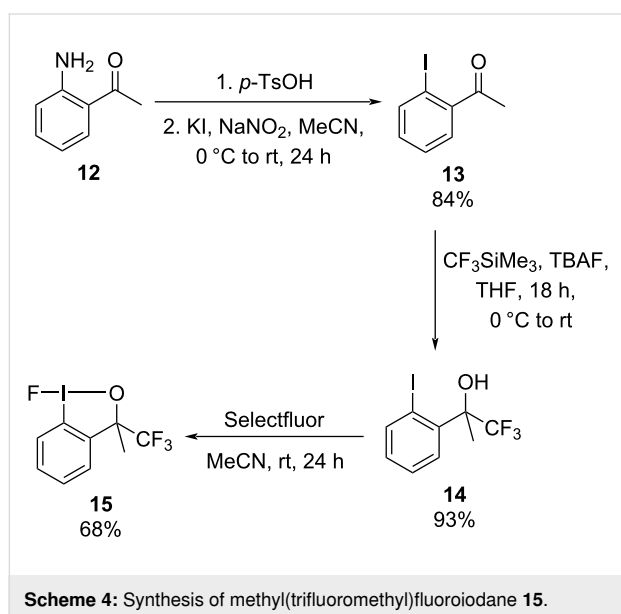
Following the successful preparation and isolation of difluoroiodane **6**, we investigated its ability to fluorinate PhMgBr as reported with iodine(V) fluoride **3** by Amey and Martin [21]. Difluoroiodane **6** was first reacted with phenylmagnesium chloride in dry toluene at 0 °C, but fluorobenzene was not formed

**Scheme 3:** Attempted oxidative fluorination of hypervalent iodine(III) amides.

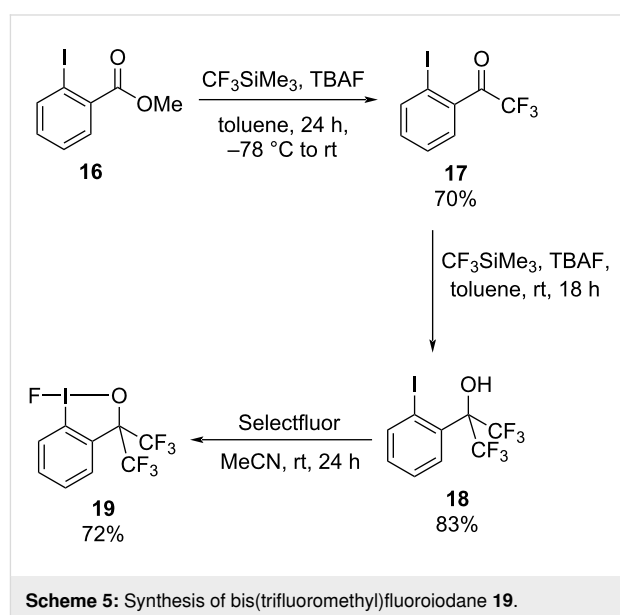
under these reaction conditions. The reaction was then repeated using phenylmagnesium bromide, but disappointingly, no fluorination was observed. The disparity in reactivity between difluoroiodane **6** and trifluoroiodane **3** towards aryl Grignard reagents could be attributed to the different relationships between the fluorine ligands on the iodine(V) centre. In difluoroiodane **6** the fluorine ligands are restricted to a *trans*-configuration because of the bicyclic carbon skeleton. Trifluoroiodane **3**, on the other hand, has both *trans*- and *cis*-configurations of the fluorine ligands which could play a key role in the reductive elimination step in the fluorination of phenylmagnesium bromide. Trifluoroiodane **3** also contains two trifluoromethyl groups in the sidearm which could alter the electronic effects significantly. We therefore decided to prepare a small series of monocyclic trifluoro(aryl)-λ⁵-iodanes, where the sidearm substituents were changed stepwise from methyl to trifluoromethyl groups, so that we also formed an analogue of Amey and Martin's monocyclic trifluoroiodane **3**.

Preparation of monocyclic trifluoro(aryl)- λ^5 -iodanes

Our investigation into the synthesis of monocyclic trifluoro(aryl)- λ^5 -iodanes began with the preparation of the key iodine(III) precursors for our oxidative fluorination protocol. Fluoroiodane **2** was already available in our laboratory [11] and the three-step synthesis of methyl(trifluoromethyl)fluoroiodane **15** is shown in Scheme 4. The first step was a diazotisation of 2'-aminoacetophenone **12** to form 2'-iodoacetophenone **13**, which was then reacted with Ruppert's reagent (CF_3SiMe_3) to afford iodoalcohol **14** in 93% yield. In the final step iodoalcohol **14** underwent an oxidative fluorination with Selectfluor at room temperature to deliver methyl(trifluoromethyl)fluoroiodane **15** in a good 68% yield after recrystallisation from toluene.



Although bis(trifluoromethyl)fluoroiodane **19** has been reported before [26–28], we developed a new synthetic route which is shown in Scheme 5. In the first step trifluoromethylketone **17** was prepared by a nucleophilic acyl substitution of methyl 2-iodobenzoate **16** with Ruppert's reagent. Ketone **17** was then reacted with an excess of Ruppert's reagent and TBAF in order to form bis(trifluoromethyl)iodoalcohol **18**, which was treated with Selectfluor in the final step to deliver bis(trifluoromethyl)fluoroiodane **19** in 72% yield.



A small series of trifluoro(aryl)- λ^5 -iodanes were successfully prepared and isolated in good yields (Table 3). Dimethyltrifluoroiodane **20** was readily formed under mild reaction conditions using 2.5 equivalents of Selectfluor at 40 °C for 24 hours. However, the introduction of trifluoromethyl groups to the

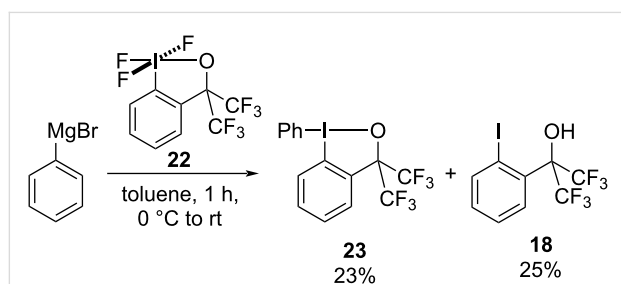
Table 3: Oxidative fluorination of monocyclic fluoroiodanes.

Entry	R/R'	Product	Selectfluor (equiv)	Temp. (°C)	Time (h)	Yield ^a (%)
1	CH ₃ /CH ₃	20	2.5	40	24	75
2	CH ₃ /CF ₃	21	3.0	60	48	78
3	CF ₃ /CF ₃	22	3.0	80	72	72

^aIsolated yield.

sidearm of the iodine(III) fluoroiodanes led to harsher oxidative fluorination conditions being required because the increased electron-withdrawing effect made the fluoroiodane precursors more resistant to oxidation. Consequently, higher temperatures, longer reaction times and more equivalents of Selectfluor were required to prepare trifluoroiodanes **21** and **22**. Trifluoro(aryl)- λ^5 -iodane **22** was also prepared directly from its iodine(I) precursor **18** in 73% isolated yield in a one-pot procedure using 5.5 equivalents of Selectfluor (see Supporting Information File 1).

Unfortunately, we were never able to replicate Amey and Martin's fluorination of phenylmagnesium bromide using bis(trifluoromethyl)trifluoroiodane **22** (Scheme 6). The major products were phenyliodane **23**, presumably a result of ligand exchange and reduction, and iodoalcohol **18**. Different solvents, temperatures and activators were investigated and the results are shown in Table S3 in Supporting Information File 1. Fluorobenzene was only ever observed in trace amounts (1–3 % spectroscopic yield) when $\text{BF}_3 \cdot \text{OEt}_2$ was added to the reaction mixture.



Scheme 6: Reaction of phenylmagnesium bromide with bis(trifluoromethyl)trifluoroiodane **22**.

X-ray crystallography and DFT calculations

The solid-state structure of difluoroiodane **6** is shown in Figure 2 and displays the expected square pyramidal geometry around the iodine atom, with only minor distortion ($\tau_5 = 0.191$). Since there were two unique molecules in the unit cell, Table 4 compares the average bond lengths and average bond angles of difluoroiodane **6** with trifluoroiodane **20**, which was reported by Togni [24], and fluoroiodane **2** [11]. The I–F bond lengths in difluoroiodane **6** (range from 1.959(4) to 1.990(4) Å) are very similar to those in trifluoroiodane **20** (range from 1.956(4) to 1.984(4) Å), but are shorter than that in fluoroiodane **2** (2.048(3) to 2.058(3) Å) suggesting that fluorine is bound more strongly to the iodine(V) centre than in iodine(III) compounds. There is a similar contraction in the I–O bond lengths when comparing iodine(V) compounds, difluoroiodane **6** (range from

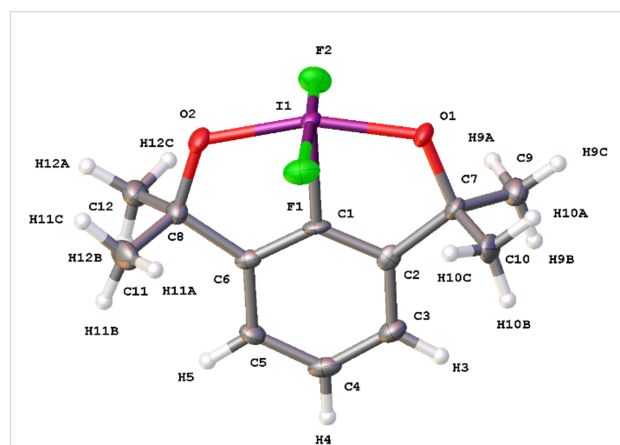


Figure 2: Molecular structure of difluoroiodane **6** showing 50% displacement ellipsoids.

Table 4: Selected average bond lengths (Å) and average bond angles ($^\circ$) with estimated standard deviations (e.s.d.s.) in parenthesis for difluoroiodane **6**, trifluoroiodane **20** and fluoroiodane **2**.

Average bond lengths (Å) and bond angles ($^\circ$)	6	20	2
C–I	2.031(6)	2.072(7)	2.089(5)
I–F	1.975(4)	1.963(4)	–
I–F'	–	1.979(4)	2.053(3)
I–O	1.986(4)	1.924(5)	2.029(3)
F'/O–I–O	161.4(2)	167.9(2)	166.7(2)
F–I–F	172.9(2)	168.5(2)	–
C–I–F	86.7(2)	85.8(3)	–
C–I–F'	–	85.8(3)	86.8(2)
C–I–O	80.7(2)	82.5(2)	80.4(2)

1.977(4) to 1.993(4) Å) and trifluoroiodane **20** (1.924(5) Å), with their respective iodine(III) precursors, **10** (2.096(2) Å) [29] and fluoroiodane **2** (2.029(3) Å). The F–I–F bond angle for difluoroiodane **6** (172.2(2)° to 173.6(2)°) deviates from 180°, but not to the same extent as seen with the aryl-IF₄ compounds (169.9(1) to 170.4(1)°) or with trifluoroiodane **20** (167.9(2)° to 169.0(2)°) [24]. On the other hand, the O–I–O bond angle for difluoroiodane **6** (161.4(2)°) is much smaller than the F'–I–O bond angles in both trifluoroiodane **20** (167.2(2)° to 168.6(2)°) and fluoroiodane **2** (166.7(2)°), presumably due to the strain caused by the two five-membered rings. Similar to trifluoroiodane **20**, there are two short intermolecular I⋯F contacts of 2.942(4) Å and 2.999(4) Å in the packing diagram of difluoroiodane **6** (see Figure S1 in Supporting Information File 1).

DFT calculations were carried out to gain further insight into the structures of iodine(V) fluorides **21** and **22** whose X-ray structures could not be obtained, and hypothetical iodine(V) amides **7a** and **7b** which could not be made. Comparisons were made with iodine(V) compounds **6** and **20**, as well as with iodine(III) compounds **2** and **19**. Geometry optimisations were performed on all the compounds using Gaussian 16 at wB97xD/cc-pvdz, with a cc-pvdz-PP basis set used for the iodine atom. The calculated bond lengths and bond angles are reported in Table 5 and are in good agreement with the solid state structures. As expected, the calculated atomic charge on iodine was much higher for the iodine(V) fluorides (1.689–1.766) than in the iodine(III) fluorides (0.957–1.009) resulting in shorter I–F and I–O bond lengths. Interestingly, there is a slightly lower charge on iodine in bicyclic iodane **6** (1.689) compared to monocyclic trifluoroiodanes **20–22** (1.738–1.766) and the ipso carbon atom is slightly less electronegative (–0.355 vs –0.414) resulting in a less polar, but slightly shorter C–I bond in

difluoroiodane **6** (2.031(6) Å) compared to trifluoroiodane **20** (2.072(7) Å). As you go across the series of monocyclic trifluoroiodanes **20** to **22**, the I–O bond length increases slightly due to the electron-withdrawing effect of the trifluoromethyl groups in the sidearms and consequently, the synergistic effect of the 3-centre-4-electron bond causes the I–F' bond length to decrease slightly. The only major difference between the bicyclic and monocyclic iodine(V) fluorides is the much smaller O–I–O bond angle (161.4(2)°) in difluoroiodane **6** compared to the F'–I–O bond angle (167.9(2)°) in **20** in the monocyclic iodanes **20–22**. In fact, DFT calculations predicted that hypothetical difluoroiodanes **7a** and **7b** containing the amide sidearms would have an even more acute N–I–N bond angle (156.6–156.9°). Furthermore, the internal chelate NCC bond angle in **7a/b** (111.7°) was calculated to be bigger than the corresponding OCC angle (108.3(5)° to 109.2(5)°) in **6** due to the sp²-hybridised carbon in **7a/b** and an sp³-hybridised carbon in **6**. This NCC bond angle (111.7°) would certainly increase the angle strain in **7a/b** and this, combined with the acute N–I–N bond angle (156.6–156.9°) caused by these two five-membered rings, could be the reason that we could not prepare these compounds.

Stability studies of hypervalent iodine(V) fluorides in solution

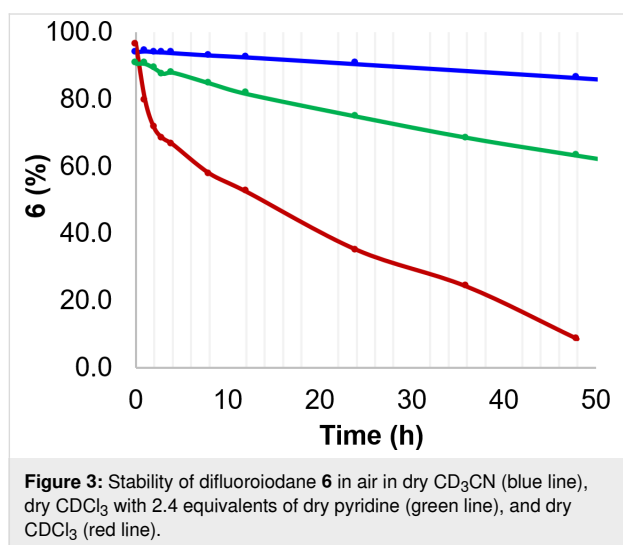
The stability of hypervalent iodine(V) fluorides **6**, **20**, **21** and **22** was studied in dry acetonitrile-*d*₃ by ¹H and ¹⁹F NMR spectroscopy over 7 days under an argon atmosphere. All four hypervalent iodine(V) fluorides were stable for the 7-day period. When the same experiment was repeated in air, iodine(V) fluorides **6**, **21** and **22** decomposed to 55–65% remaining after 7 days presumably due to the moisture in the air, whereas trifluoroiodane **20** was less stable with only 37% remaining. Difluoro-

Table 5: Comparing properties of hypervalent iodine(V) fluorides with hypervalent iodine(III) fluorides **2** and **19**^a.

	d(C–I) (Å)	d(I–F) (Å)	d(I–F') (Å)	d(I–O/N) (Å)	q _C	q _I	q _F	q _{F'}	q _{O/N}	θ _{F–I–F} (°)	θ _{O–I–O/F'/ N–I–N} (°)
6	2.04	2.00 ^b	–	2.03	–0.355	1.689	–0.460	–	–0.561	173.6	161.1
7a	2.06	2.00	–	2.12	–0.312	1.668	–0.426	–	–0.609	175.9	156.6
7b	2.05	1.99 ^b	–	2.12	–0.314	1.667	–0.444	–	–0.591	176.7	156.9
20	2.09	1.98 ^b	1.99	1.99	–0.419	1.738	–0.453	–0.449	–0.556	171.8	168.8
21	2.09	1.98 ^c	1.98	2.01	–0.415	1.753	–0.445 ^d	–0.439	–0.550	171.7	168.6
22	2.10	1.97 ^b	1.97	2.03	–0.407	1.766	–0.438	–0.428	–0.540	171.4	168.5
2	2.10	–	2.04	2.07	–0.403	0.957	–	–0.490	–0.574	–	167.9
19	2.10	–	2.02	2.09	–0.387	1.009	–	–0.469	–0.552	–	167.8

^aCalculations performed at wB97xD/cc-pvdz, with a cc-pvdz-PP basis set used for the iodine atom. C refers to ipso carbon atom, F and F' refers to fluorine atom bound to iodine. ^bStructure is nearly symmetric about F–I–F' (mirror plane). ^cAverage between 1.99 and 1.97. ^dAverage between –0.441 and –0.449.

iodane **6** was also stable in dry chloroform- d_1 under argon over 7 days, but it decomposed completely to iodosyl **9** after just 48 hours in dry chloroform- d_1 in air (red line in Figure 3). The difference in the stability of difluoroiodane **6** in CDCl_3 and CD_3CN was attributed to the ability of acetonitrile to coordinate to the iodine(V) centre. Stabilisation via halogen bonding is well-established in hypervalent iodine(III) compounds and Dutton showed that pyridine formed a weak complex with dichloriodobenzene via halogen bonding [30–32]. We therefore added dry pyridine (2.4 equivalents) to difluoroiodane **6** in CDCl_3 to help stabilise the iodine(V) centre and the rate of decomposition was reduced significantly (green line in Figure 3).



The hydrolysis of the four hypervalent iodine(V) fluorides was also investigated in acetonitrile- d_3 by adding 5 equivalents of water. All four compounds decomposed to their corresponding iodosyl compounds and the order of stability is shown in Figure 4. Difluoroiodane **6**, containing two 5-membered rings, was the most stable iodine(V) fluoride whereas monocyclic trifluoroiodane **20** was the least stable and decomposed completely within the first minute. As expected, the stability of the monocyclic trifluoroiodanes **21** and **22** was increased by the stepwise incorporation of the trifluoromethyl groups into the sidearm, but trifluoroiodane **22** was less stable than bicyclic difluoro(aryl)- λ^5 -iodane **6**.

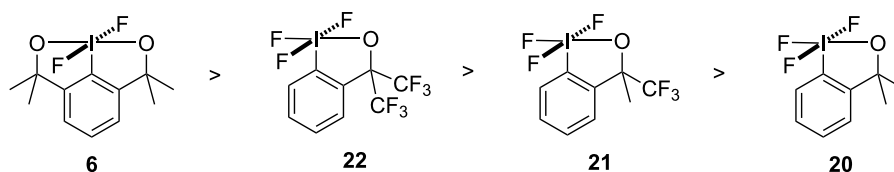


Figure 4: Order of hydrolytic stability for the four hypervalent iodine(V) fluorides.

Conclusion

In summary, we have developed a new strategy using Selectfluor for the convenient preparation and isolation of hypervalent iodine(V) fluorides in good yields (72–90%). Unfortunately, none of the iodine(V) fluorides reacted with phenylmagnesium bromide to form fluorobenzene and we were never able to repeat Amey and Martin's fluorination of phenylmagnesium bromide. A solid-state structure of **6** and DFT calculations on **6** and **20–22** gave insights into the geometries of the iodine(V) fluorides compared to the iodine(III) precursors. DFT results also suggested a possible reason for not being able to make iodine(V) amides **7a** and **7b**. An investigation into the hydrolysis of the four hypervalent iodine(V) fluorides revealed that bicyclic difluoro(aryl)- λ^5 -iodane **6** was more stable than monocyclic trifluoro(aryl)- λ^5 -iodanes **20–22** due to the incorporation of the second 5-membered ring in the 3-centre-4-electron bond.

Experimental

Dioxoiodane **10** (0.58 g, 1.8 mmol), Selectfluor (0.97 g, 2.7 mmol) and dry acetonitrile (10 mL) were charged to a dry Schlenk flask under a nitrogen atmosphere. The flask was sealed and heated to 40 °C for 24 hours. After cooling the reaction mixture to room temperature, the solvent was removed in vacuo to afford a crude orange solid. The orange solid was extracted with dry dichloromethane (3×5 mL) under a nitrogen atmosphere and the dichloromethane was removed in vacuo to afford difluoroiodane **6** as a pale orange solid (0.58 g, 90%).

Supporting Information

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC: 2351949 and 2351950.

Supporting Information File 1

Experimental procedures, characterisation data, DFT calculations and ^1H , ^{13}C and ^{19}F NMR spectra and crystallographic data.

[<https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-20-157-S1.pdf>]

Funding

SMGD and AMS thank the School of Chemistry, University of Leicester, for their generous support. AMS also thanks the EPSRC for research grant EP/W02151X/1.

ORCID® iDs

Samuel M. G. Dearman - <https://orcid.org/0009-0003-5421-1647>

Yang Li - <https://orcid.org/0000-0002-5719-9044>

Alison M. Stuart - <https://orcid.org/0000-0001-5984-4919>

Data Availability Statement

All data that supports the findings of this study is available in the published article and/or the supporting information to this article.

References

- Inoue, M.; Sumii, Y.; Shibata, N. *ACS Omega* **2020**, *5*, 10633–10640. doi:10.1021/acsomega.0c00830
- Han, J.; Remete, A. M.; Dobson, L. S.; Kiss, L.; Izawa, K.; Moriwaki, H.; Soloshonok, V. A.; O'Hagan, D. *J. Fluorine Chem.* **2020**, *239*, 109639. doi:10.1016/j.jfluchem.2020.109639
- Wang, Z.-X.; Livingstone, K.; Hümpel, C.; Daniliuc, C. G.; Mück-Lichtenfeld, C.; Gilmour, R. *Nat. Chem.* **2023**, *15*, 1515–1522. doi:10.1038/s41557-023-01344-5
- Häfliger, J.; Ruyet, L.; Stübke, N.; Daniliuc, C. G.; Gilmour, R. *Nat. Commun.* **2023**, *14*, 3207. doi:10.1038/s41467-023-38957-w
- Yu, Y.-J.; Schäfer, M.; Daniliuc, C. G.; Gilmour, R. *Angew. Chem., Int. Ed.* **2023**, *62*, e202214906. doi:10.1002/anie.202214906
- Neufeld, J.; Daniliuc, C. G.; Gilmour, R. *Helv. Chim. Acta* **2023**, *106*, e202200183. doi:10.1002/hlca.202200183
- Meyer, S.; Göbel, L.; Livingstone, K.; Roblick, C.; Daniliuc, C. G.; Gilmour, R. *Tetrahedron* **2022**, *126*, 132925. doi:10.1016/j.tet.2022.132925
- Neufeld, J.; Stünkel, T.; Mück-Lichtenfeld, C.; Daniliuc, C. G.; Gilmour, R. *Angew. Chem., Int. Ed.* **2021**, *60*, 13647–13651. doi:10.1002/anie.202102222
- Doobary, S.; Sedikides, A. T.; Caldora, H. P.; Poole, D. L.; Lennox, A. J. *Angew. Chem., Int. Ed.* **2019**, *58*, 1155–1160. doi:10.1002/anie.201912119
- Doobary, S.; Poole, D. L.; Lennox, A. J. *J. Org. Chem.* **2021**, *86*, 16095–16103. doi:10.1021/acs.joc.1c01946
- Geary, G. C.; Hope, E. G.; Singh, K.; Stuart, A. M. *Chem. Commun.* **2013**, *49*, 9263–9265. doi:10.1039/c3cc44792h
- Geary, G. C.; Hope, E. G.; Stuart, A. M. *Angew. Chem., Int. Ed.* **2015**, *54*, 14911–14914. doi:10.1002/anie.201507790
- Minhas, H. K.; Riley, W.; Stuart, A. M.; Urbonaite, M. *Org. Biomol. Chem.* **2018**, *16*, 7170–7173. doi:10.1039/c8ob02236d
- Abudken, A. M. H.; Hope, E. G.; Singh, K.; Stuart, A. M. *Org. Biomol. Chem.* **2020**, *18*, 6140–6146. doi:10.1039/d0ob01401j
- Riley, W.; Jones, A. C.; Singh, K.; Browne, D. L.; Stuart, A. M. *Chem. Commun.* **2021**, *57*, 7406–7409. doi:10.1039/d1cc02587b
- Ilchenko, N. O.; Tasch, B. O. A.; Szabó, K. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 12897–12901. doi:10.1002/anie.201408812
- Yuan, W.; Eriksson, L.; Szabó, K. J. *Angew. Chem., Int. Ed.* **2016**, *55*, 8410–8415. doi:10.1002/anie.201602137
- Ilchenko, N. O.; Cortés, M. A.; Szabó, K. J. *ACS Catal.* **2016**, *6*, 447–450. doi:10.1021/acscatal.5b02022
- Ulmer, A.; Brunner, C.; Arnold, A. M.; Pöthig, A.; Gulder, T. *Chem. – Eur. J.* **2016**, *22*, 3660–3664. doi:10.1002/chem.201504749
- Zhao, P.; Wang, W.; Gulder, T. *Org. Lett.* **2023**, *25*, 6560–6565. doi:10.1021/acs.orglett.3c02384
- Amey, R. L.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5294–5299. doi:10.1021/ja00512a030
- Nguyen, T. T.; Amey, R. L.; Martin, J. C. *J. Org. Chem.* **1982**, *47*, 1024–1027. doi:10.1021/jo00345a026
- Gruber, S.; Ametamey, S. M.; Schibli, R. *Chem. Commun.* **2018**, *54*, 8999–9002. doi:10.1039/c8cc04558e
- Häfliger, J.; Pitts, C. R.; Bornemann, D.; Käser, R.; Santschi, N.; Charpentier, J.; Otth, E.; Trapp, N.; Verel, R.; Lüthi, H. P.; Togni, A. *Chem. Sci.* **2019**, *10*, 7251–7259. doi:10.1039/c9sc02162k
- Ullah, K.; Kordnezhadian, R.; Demaerel, J.; De Borggraeve, W. M.; Ismalaj, E. *J. Fluorine Chem.* **2024**, *275*, 110276. doi:10.1016/j.jfluchem.2024.110276
- Chai, J.; Ding, W.; Wu, J.; Yoshikai, N. *Chem. – Asian J.* **2020**, *15*, 2166–2169. doi:10.1002/asia.202000653
- Cvengroš, J.; Stolz, D.; Togni, A. *Synthesis* **2009**, 2818–2824. doi:10.1055/s-0029-1217406
- Milzarek, T. M.; Ramirez, N. P.; Liu, X.-Y.; Waser, J. *Chem. Commun.* **2023**, *59*, 12637–12640. doi:10.1039/d3cc04525k
- Gao, W.-C.; Zhang, C. *Tetrahedron Lett.* **2014**, *55*, 2687–2690. doi:10.1016/j.tetlet.2014.03.034
- Pinto de Magalhães, H.; Togni, A.; Lüthi, H. P. *J. Org. Chem.* **2017**, *82*, 11799–11805. doi:10.1021/acs.joc.7b01716
- Matoušek, V.; Václavík, J.; Hájek, P.; Charpentier, J.; Blastik, Z. E.; Pietrasiak, E.; Budinská, A.; Togni, A.; Beier, P. *Chem. – Eur. J.* **2016**, *22*, 417–424. doi:10.1002/chem.201503531
- Poynder, T. B.; Chamorro Orué, A. I.; Tania; Sharp-Bucknall, L.; Flynn, M. T.; Wilson, D. J. D.; Athukorala Arachchige, K. S.; Clegg, J. K.; Dutton, J. L. *Chem. Commun.* **2021**, *57*, 4970–4973. doi:10.1039/d1cc01567b

License and Terms

This is an open access article licensed under the terms of the Beilstein-Institut Open Access License Agreement (<https://www.beilstein-journals.org/bjoc/terms>), which is identical to the Creative Commons Attribution 4.0 International License (<https://creativecommons.org/licenses/by/4.0>). The reuse of material under this license requires that the author(s), source and license are credited. Third-party material in this article could be subject to other licenses (typically indicated in the credit line), and in this case, users are required to obtain permission from the license holder to reuse the material.

The definitive version of this article is the electronic one which can be found at:
<https://doi.org/10.3762/bjoc.20.157>