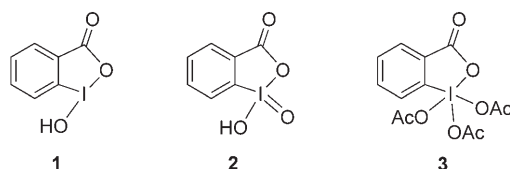


Tetrafluoro-IBA and-IBX: Hypervalent Iodine Reagents**

Robert D. Richardson, Jameel M. Zayed, Sabine Altermann, Daniel Smith, and Thomas Wirth*

Hypervalent iodine reagents^[1] especially cyclic iodanes and periodanes, such as IBA (1), IBX (2), and Dess–Martin

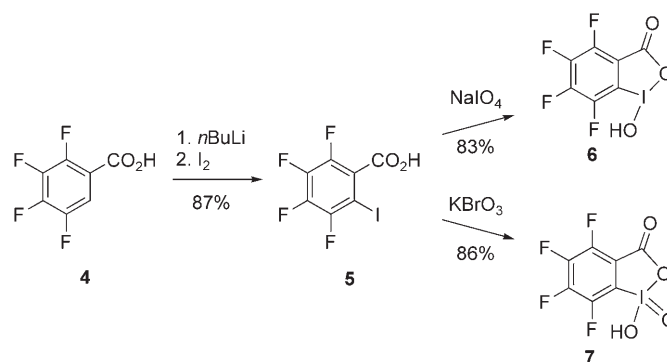


periodinane (DMP, 3) are much used synthetic reagents with broad application in synthesis.^[2] DMP (3) has been used widely in the selective oxidation of alcohols to carbonyl compounds and in cascade reactions.^[3] IBX (2) can mediate many useful transformations^[2b] such as the introduction of an α,β double bond to carbonyl compounds,^[4] oxidation of benzylic methylene and methyl groups, and cyclizations by single-electron-transfer processes.^[5]

Unfortunately, IBX (2) has several drawbacks. It has been reported to be explosive,^[6] it has low solubility so it is often limited to use in polar solvents such as DMSO,^[3–5] and the conditions for many of the IBX-mediated reactions often involve high temperatures. Some attempts—such as the addition of additives to IBX (2) for its stabilization^[7] or for increasing the reactivity,^[4] the functionalization of the arene moiety to improve solubility in organic solvents^[8] or water,^[9] and the attachment to a solid support^[10]—have solved some of these problems but rarely all of them. Theoretical investigations to improve reactivity have also been published.^[11] IBA (1) and its derivatives are seldom used in synthesis owing to the decreased reactivity of these reagents as oxidants, especially as hypernucleofuges.^[12] Inspired by the increased solubility and reactivity of [bis(trifluoroacetoxy)iodo]pentafluorobenzene^[13] and other hypervalent iodine reagents with fluorine side chains,^[14] we proposed that fluorination of the arene in the parent 2-iodobenzoic acid should solve many of

the problems associated with cyclic iodanes. In this communication, we report what we believe to be the first hypervalent derivatives of 2,3,4,5-tetrafluoro-6-iodobenzoic acid (5) and discuss their structures and reactivities.

The parent 2,3,4,5-tetrafluoro-6-iodobenzoic acid (5) has been reported as a product of iodolysis of organomercury compounds.^[15] Use of toxic reagents in and the poor yield of this procedure led us to pursue our own synthesis of this compound. Treatment of commercial 2,3,4,5-tetrafluorobenzoic acid (4) with excess *n*-butyllithium in tetrahydrofuran at low temperature (found to be necessary) followed by reaction with elemental iodine gave 5 in good yield regardless of scale (Scheme 1). Acid 5 was easily purified by trituration under hexane.



Scheme 1. Preparation of 5–7.

Oxidation of acid 5 to the λ^3 -iodane 6 (FIBA) proved to be easy using a modification of conditions previously reported for the preparation of 1.^[16] Refluxing acid 5 with one equivalent of sodium periodate in trifluoroacetic acid/water (1:1) gave 6 in good yield and excellent purity according to ¹⁹F NMR and [¹⁹F]¹³C NMR spectroscopy and by elemental analysis (Scheme 1). Use of excess sodium periodate led to the formation of some iodine(V) reagent that could not be separated. This seems to be remarkable as IBA tends not to be overoxidized under these reaction conditions. λ^5 -Iodane 7 (FIBX) was obtained in high yield and purity (¹⁹F NMR and [¹⁹F]¹³C NMR spectroscopy and elemental analysis) by treatment of the parent iodobenzoic acid 5 with potassium bromate in dilute sulfuric acid, as previously reported for the preparation of IBX (2).^[17] Treatment of iodide 5 with fuming nitric acid in trifluoroacetic anhydride as described for the oxidation of pentafluoriodobenzene to the corresponding bis(trifluoroacetoxy)iodo compound^[18] gave the iodine(III) reagent 6 but in lower purity. Attempts to oxidize iodoarene 5 with either trifluoroperacetic acid^[19] or dimethyldioxirane^[20] were unsuccessful, and the starting material was recovered unchanged. We were unable to convert FIBX (7) to the fluorinated Dess–Martin periodinane analogue. Reaction

[*] Dr. R. D. Richardson, J. M. Zayed, S. Altermann, D. Smith, Prof. Dr. T. Wirth
School of Chemistry
Cardiff University
Park Place, Cardiff CF103AT (UK)
Fax: (+44) 29-2087-6968
E-mail: wirth@cf.ac.uk
Homepage: <http://www.cf.ac.uk/chem/wirth>

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with acetic acid/acetic anhydride led to complete reduction to the iodine(I) compound, and reaction with trifluoroacetic anhydride resulted in a complex mixture of compounds judged by the ^{19}F NMR spectrum.

The $\{^{19}\text{F}\}$ -decoupled ^{13}C NMR spectra of **5–7** show a downfield shift of the carbon atom attached to iodine of 23.7 ppm on oxidation from iodine(I) to iodine(III) and a further downfield shift of 17.1 ppm on oxidation to iodine(V) (Table 1). This compares to downfield shifts of 26.4 ppm and a further 26.2 ppm, respectively, for the same carbon atom in the non-fluorinated series (Table 1).^[21] A similar trend of the

Table 1: ^{13}C NMR shifts [ppm] of selected carbon atoms in cyclic iodanes.

	I ^I	I ^{III}	I ^V
$\delta(\text{C}=\text{O})$ ^[b]	5: 164.1	6: 162.4	7: 162.6
$\delta(\text{C}=\text{O})$	168.7 ^[a] ^[24]	1: 167.7 ^[24]	2: 167.5 ^[23]
$\delta(\text{C-I})$ ^[b]	5: 77.1	6: 100.8	7: 117.9
$\delta(\text{C-I})$	94.0 ^[a] ^[24]	1: 120.4 ^[24]	2: 146.6 ^[23]
$\Delta\delta(\text{C}=\text{O})$ to I ^[b]	0.0	−1.7	−1.5
$\Delta\delta(\text{C}=\text{O})$ to I ^I	0.0	−0.4	−0.6
$\Delta\delta(\text{C-I})$ to I ^[b]	0.0	+23.7	+40.8
$\Delta\delta(\text{C-I})$ to I ^I	0.0	+26.4	+52.6

[a] 2-Iodobenzoic acid. [b] Tetrafluoro derivatives.

^{13}C NMR shifts of the iodine-bearing carbon atom is also seen upon oxidation of non-cyclic aryl iodides to their corresponding iodine(III) and iodine(V) derivatives.^[21] This already allows a clear distinction between the different oxidation states of the iodine using ^{13}C NMR shift values. In contrast, the ^{13}C NMR shifts of the carbonyl carbon atom are independent of the iodine oxidation state. The IR stretching frequencies of the carbonyl groups were initially used to assign the cyclic structures of IBA (**1**) and IBX (**2**).^[22] The C=O frequency of **5**^[15] is 1705 cm^{-1} ; upon oxidation to iodine(III) this frequency changes to 1643 cm^{-1} (**6**) and after oxidation to iodine(V) to 1661 cm^{-1} (**7**). The values for 2-iodobenzoic acid,^[23] IBA (**1**),^[22,23] and IBX (**2**)^[23] are 1680, 1620, and 1640 cm^{-1} , respectively. These values indicate that the replacement of the four hydrogen atoms by fluorine lead to a difference in the carbonyl frequencies by approximately 20 cm^{-1} . IR spectra can therefore serve to quickly determine the oxidation state of 2-iodocarboxylic acids.

The structure of FIBA (**6**) could be assigned unambiguously by single-crystal X-ray diffraction (Figure 1).^[25] The structure is very similar to that of IBA (**1**)^[26] except that the C7-I1-O3 angle is enlarged (97° compared with 89° in **1**) in order to accommodate the intramolecular O3-H1...F4 hydrogen bond. The calculated structure of **6** at the HF/6-31G(d,p) level^[27] using the LANL2DZ(d,p) for iodine,^[28] shows a preference for a conformation with this intramolecular hydrogen bond, although this structure is slightly distorted from planarity.

The acidity of FIBA (**6**) and FIBX (**7**) in comparison to that of **1** and **2**, respectively, is most likely to be increased, but it can be assumed that this result in changes in the mechanisms of one-step oxidation processes.^[29] The increased

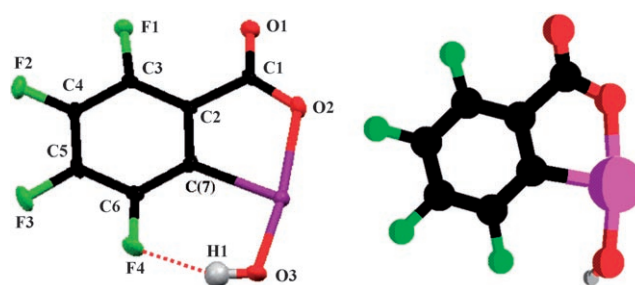
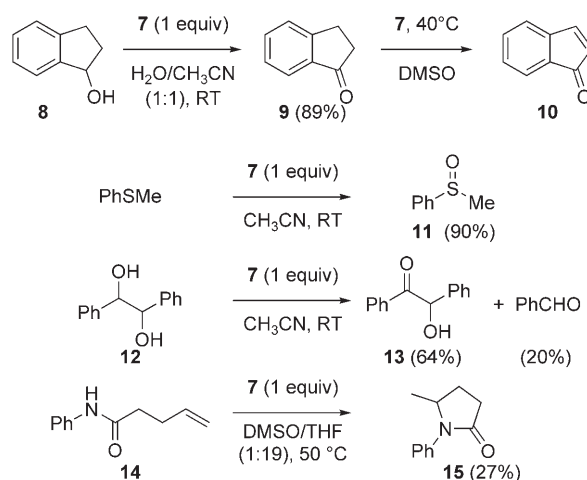


Figure 1. X-ray crystal structure (left) and calculated structure (right) of FIBA (**6**).

acidity might, however, have an effect on acid-sensitive subsequent reactions.^[30] FIBX (**7**) is more soluble in water than IBX (**2**), but the solubility in fluorinated solvents such as perfluorohexane is negligible. The reactivity of FIBX (**7**) seems to be increased compared to that of IBX (**2**), and several reactions confirm this observation.

It is known that IBX reacts with THF in a radical pathway at temperatures above 80 °C.^[5a] We investigated the reactivity of FIBX (**7**) by monitoring the ^{19}F NMR spectrum of a solution of **7** in THF at different temperatures and found that it reacts with THF at only 40 °C.

Simple oxidation reactions can be performed as efficiently with **7** as with IBX with the advantage of not having to use DMSO as a solvent. The oxidation of 2-indanol (**8**) to indanone **9** can be performed at room temperature in water/acetonitrile (1:1) and is complete within 4 h (Scheme 2). No further oxidation to the α,β -unsaturated indanone **10** is observed in this solvent. The reaction is faster (30 min) in DMSO, and even at room temperature the formation of **10** can be detected. Owing to the reactivity of FIBA (**6**) generated in this oxidation (see Scheme 3), side reactions at the α position of **9** are observed as well. Other solvents can be used for oxidation reactions as well: sulfoxide **11** can be prepared in 90% yield by oxidation of thioanisole in acetonitrile. There is no need to add a quarternary ammonium salt to increase the solubility and reactivity,^[7b,31] and the corresponding sulfone is not detected. In contrast to IBX,^[32] FIBX (**7**) is able to cleave diols such as **12**; benzoin **13** and



Scheme 2. Reactions performed with FIBX (**7**).

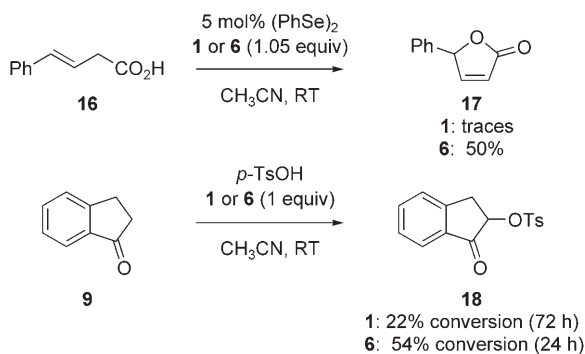
benzaldehyde were obtained in a reaction in acetonitrile at room temperature. FIBX can also serve as a reagent to induce the radical cyclization of unsaturated amides such as **14**. The cyclization is slightly faster than with IBX and produces the lactam **15**. After 6 h reaction at 90 °C the conversion with FIBX was 35 % and 30 % with IBX. However, the oxidation of THF by FIBX is a significant pathway.

Many new reactions described in recent literature are mediated by IBX. For example, α -hydroxylation of α -alkynylketones,^[33] synthesis of *Z*-enediones,^[34] aromatization of dihydropyridines,^[35] oxidative Passerini reactions,^[36] cleavage of diols,^[37] coupling of alkynes,^[38] and oxidation of aldehydes to nitriles.^[39] The effect on some of these reactions of using FIBX instead of IBX might be very interesting.

Reactions with IBA (**1**) are much less common in organic synthesis owing to its low reactivity.^[40] FIBA (**6**), however, can be used advantageously. The diphenyl diselenide catalyzed cyclization of **16** to the butenolide **17** can be achieved with FIBA (**6**) (Scheme 3),^[41] while IBA (**1**) is not reactive in this system. The same is true for α -functionalizations: indanone **9** can be oxytosylated in the α position using FIBA (**6**) to give **18** in moderate yields while IBA leads to much lower conversions.

A highly attractive feature of all these oxidation reactions is the possibility to directly measure the composition of oxidant in the reaction mixture by ¹⁹F NMR spectroscopy. As deuterated solvents are not necessary for these measurements, the reaction mixtures can be analyzed directly. It is interesting to note that in many oxidation reactions using FIBX, the ¹⁹F NMR spectrum shows the presence of only iodine(V) and iodine(I) compounds. This contrasts with IBX and the Dess–Martin periodane where IBA (**1**) and its derivatives can be isolated as products.

The novel reagents FIBA (**6**) and FIBX (**7**) offer advantages for some of these processes which now can be performed in common organic solvents. As a result of the increased reactivity of these reagents new transformations or catalytic reactions may be possible.^[42] Derivatives of **6** might also provide an alternative route to tetrafluorobenzene.^[43] Studies into comparative reactivities (experimentally and computationally) are in progress.



Scheme 3. Reactions performed with FIBA (**6**).

Experimental Section

Synthesis of **5**: *n*-Butyllithium (68 mL, 2.5 M in hexanes, 170 mmol) was added to a solution of **4** (15 g, 77 mmol) in anhydrous

tetrahydrofuran (250 mL) at –78 °C. The resulting suspension was stirred for 3 h at –78 °C. Then a solution of iodine (23 g, 90 mmol) in anhydrous tetrahydrofuran (50 mL) was added slowly until the brown color of the iodine persisted in the solution. The resulting solution was warmed to room temperature and more of the iodine solution could be added if the brown color disappeared. The reaction was quenched by dropwise addition of saturated aqueous sodium hydrogen sulfite solution until the brown color faded, and the reaction mixture was concentrated under reduced pressure. The crude product was triturated under hexane (100 mL) for 4 h, and solid acid **5** (18.2 g, 57 mmol, 74 %) was collected by filtration as a powder, washed with hexane (30 mL), and dried under reduced pressure. Concentration of the filtrate under reduced pressure and trituration under hexane (20 mL) gave further acid **5** (3.2 g, 10 mmol, 13 %; total yield: 21.4 g, 67 mmol, 87 %). M.p. 125–126 °C; ¹⁹F NMR (283 MHz, [D₆]DMSO): δ_F = –116.0 (1F, dd, *J* = 24.3, 6.9 Hz, ICCF), –140.5 (1F, dd, *J* = 20.8, 10.4 Hz, HO₂CCCCF), –152.4 (1F, t, *J* = 20.8 Hz, CFCFCFCF), –154.2 ppm (1F, t, *J* = 24.3 Hz, CFCFCFCF); [¹⁹F]¹³C NMR (76 MHz, [D₆]DMSO) δ_F = 164.1 (C=O), 149.7 (CC=O), 147.2 (CF), 143.7 (CF), 139.8 (CF), 125.6 (CF), 77.1 ppm (CI).

Synthesis of FIBA (**6**): Following a modification of a published procedure,^[16] a solution of acid **5** (1.60 g, 5 mmol) and sodium periodate (1.1 g, 5.1 mmol) in trifluoroacetic acid (10 mL) and distilled water (10 mL) was heated at reflux for 3 h, then cooled to room temperature. The resulting suspension was concentrated under reduced pressure, poured into ice-cold water (5 mL), and **6** (1.40 g, 4.17 mmol, 83 %) was collected by filtration, washed with ice-cold water (5 mL) and hexane (10 mL), and dried under reduced pressure. A sample for X-ray crystallography and elemental analysis was recrystallized from MeCN/DMSO (approx. 4:1) as prisms. M.p. 179–180 °C; IR: $\tilde{\nu}$ = 3060, 1643, 1619, 1596, 1496, 1349, 1055, 597; ¹⁹F NMR (283 MHz, [D₆]DMSO): δ_F = –140.0 (1F, dd, *J* = 24.3, 10.4 Hz, CFCFCFCF), –140.1 to –140.5 (1F, m, CFCFCFCF), 148.0 (1F, td, *J* = 24.3, 10.4 Hz, CFCFCFCF), –151.1 ppm (1F, t, *J* = 24.3 Hz, CFCFCFCF); [¹⁹F]¹³C NMR (76 MHz, [D₆]DMSO) δ_F = 162.4 (C=O), 148.5 (CF), 148.7 (CF), 144.0 (CC=O), 141.8 (CF), 118.5 (CF), 100.8 (CI) ppm; MS (EI) *m/z* (%): 320(8), 376(28), 177(18), 148(23), 127(36), 99(53), 44(100); Elemental analysis for C₇HF₄IO₃: calcd. C 25.01, H 0.3; found C 24.93, H 0.25.

Synthesis of FIBX (**7**): Following a modification of the procedure of Mullins,^[17] acid **5** (1.92 g, 6 mmol) was added portionwise to a solution of potassium bromate (2.2 g, 13.2 mmol, 2.1 equiv) in aqueous sulfuric acid (20 mL, 2 M) at 65 °C over 15 min. The resulting suspension was then stirred at 75 °C for 3 h (Caution! Bromine vapor is liberated) during which the reaction mixture turned orange, then returned to a white suspension in a colorless solution. The reaction mixture was cooled in ice/salt mixture until the internal temperature was below –5 °C. The solution was filtered, and the filtrate washed with ice-cold water (2 × 10 mL) and ethanol (10 mL), and dried under reduced pressure to yield **7** (1.81 g, 5.14 mmol, 86 %) as a powder. M.p. 203–204 °C (decomp.); IR: $\tilde{\nu}$ = 3425, 1660, 1637, 1501, 1472, 1360, 1061, 797 cm^{–1}; ¹⁹F NMR (283 MHz, [D₆]DMSO): δ_F = –137.8 to –138.3 (1F, m, CFCFCFCF), –138.6 to –139.0 (1F, m, CFCFCFCF), –147.2 (1F, td, *J* = 24.3, 8.4 Hz, CFCFCFCF), –151.1 ppm (1F, td, *J* = 24.3, 8.6 Hz, CFCFCFCF); [¹⁹F]¹³C NMR (76 MHz, [D₆]DMSO): δ_F = 162.6 (C=O), 147.6 (CF), 145.4 (CF), 143.6 (CC=O), 143.0 (CF), 131.6 (CF), 117.9 ppm (CI); MS (EI) *m/z* (%): 320(5), 303(8), 176(16), 148(27), 127(32), 99(34), 84(44), 49(100); Elemental analysis for C₇HF₄IO₄·H₂O: calcd. C 22.72, H 0.81, I 34.3; found C 22.66, H 0.23, I 34.52.

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